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# PRIORITY SUBSTANCES LIST ASSESSMENT REPORT

## Inorganic Chloramines

Canada

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*Canadian Environmental Protection Act, 1999*

# PRIORITY SUBSTANCES LIST ASSESSMENT REPORT

# Inorganic Chloramines

Environment Canada
Health Canada

March 2001

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# List of Acronyms and Abbreviations

| | |
|---|---|
| CAC | combined available chlorine |
| CAS | Chemical Abstracts Service |
| CEPA | *Canadian Environmental Protection Act* |
| CEPA 1999 | *Canadian Environmental Protection Act, 1999* |
| CPO | chlorine-produced oxidants |
| CRC | combined residual chlorine |
| CTV | Critical Toxicity Value |
| DNA | deoxyribonucleic acid |
| DPD | N,N-diethyl-p-phenylenediamine |
| $EC_{50}$ | median effective concentration |
| EEC | Estimated Environmental Concentration |
| EEV | Estimated Exposure Value |
| ENEV | Estimated No-Effects Value |
| FAC | free available chlorine |
| FAS | ferrous ammonium sulfate |
| FRC | free residual chlorine |
| FVRD | Fraser Valley Regional District |
| HPLC | high-pressure liquid chromatography; high-performance liquid chromatography |
| $LC_{50}$ | median lethal concentration |
| $LT_{50}$ | median lethal time |
| NOAEC | No-Observed-Adverse-Effect Concentration |
| pH | negative logarithm of the hydrogen ion concentration |
| pK | negative logarithm of the acid dissociation constant |
| PSL | Priority Substances List |
| PSL2 | Second Priority Substances List |
| RNA | ribonucleic acid |
| STP | standard temperature and pressure |
| THM | trihalomethane |
| TRC | total residual chlorine |
| TRO | total residual oxidant |
| WTP | water treatment plant |
| WWTP | wastewater treatment plant |

# SYNOPSIS

Inorganic chloramines consist of three chemicals that are formed when chlorine and ammonia are combined in water: monochloramine ($NH_2Cl$), dichloramine ($NHCl_2$) and trichloramine ($NCl_3$). Inorganic chloramines, free chlorine and organic chloramines are chemically related and are easily converted into each other; thus, they are not found in isolation. Chloramines and free chlorine are released to the Canadian environment by municipal and industrial sources. They are used to disinfect drinking water and wastewaters and to control biological fouling in cooling water systems and at the intakes and outlets of utilities and industries (e.g., for zebra mussel control). When chlorination of fresh water or effluent occurs in the presence of ammonia, monochloramine usually forms; dichloramine may also form to a lesser degree, depending on the characteristics of the raw water or influent (e.g., pH, molar ratio of hypochlorous acid to ammonia, temperature) and the chlorine contact time. Conditions favouring the formation of trichloramine are rare. Organic chloramines are also produced if certain organic nitrogen compounds, including amino acids and nitrogen heterocyclic aromatics, are present.

This risk assessment focused on inorganic chloramines, but also acknowledged the combined presence of free residual chlorine (FRC) and organic chloramines. Risk assessments of organic chloramines and FRC were beyond the scope of this assessment.

In 1996, approximately 6.9 million Canadians were serviced by chloraminated drinking water. An estimated 250 000 kg of total residual chlorine (TRC) were released to Canadian surface waters and soils from potable water sources in 1996. In 1996, approximately 173 municipal wastewater treatment plants (WWTPs) chlorinated effluent and did not dechlorinate before discharge. These facilities released approximately 1.3 million kilograms of TRC to surface waters. In 1996, there were at least 43 industrial facilities chlorinating effluents or cooling waters or chlorinating to control biological fouling and not dechlorinating prior to discharge. Facilities involved in the control of biofouling released approximately 142 000 kg of TRC to surface waters. Cooling and other industrial sources released a total of approximately 91 000 kg of TRC to the Canadian environment in 1996. Many municipal and industrial facilities dechlorinate their effluents, and hence, do not release measurable concentrations of chloramines and free chlorine to the environment.

Inorganic chloramines are not persistent, but they are more persistent than FRC compounds. In surface waters, the available data suggest that inorganic chloramines have half-lives ranging from 1 minute to 23 days, depending on the conditions. Inorganic chloramine concentrations in the environment have been measured only in surface waters, and usually near the point of entry, because of their limited persistence. Since they are released to surface waters and have limited persistence, the assessment focused on an evaluation of risk to sensitive aquatic life near point sources. Acute and subacute effects were assessed in receptor organisms. The potential risks to microorganisms and soil processes were also acknowledged. Based on the available evidence, adverse effects on soil microorganisms and associated soil processes from inorganic chloramines were considered unlikely.

The aquatic toxicity of inorganic chloramines is dependent on biological species, chloramine compounds, presence of FRC and organic chloramines, temperature, exposure duration and life stage of the biological species. A critical review of environmental toxicity data for inorganic chloramines was conducted. Using a meta-analysis approach, a lower-boundary concentration line that bounded the acute toxicity data for all species was developed, sensitive species were identified and data gaps were

outlined. To fill the data gaps, toxicity tests on freshwater fish (juvenile chinook salmon, *Oncorhynchus tshawytscha*), freshwater invertebrates (*Ceriodaphnia dubia* and *Daphnia magna*) and marine invertebrates (*Amphiporeia virginiana* and *Eohaustorius washingtonianus*) were undertaken, and time-to-lethality (e.g., $LT_{100}$, $LT_{50}$, $LT_{20}$, $LT_0$) reference lines were determined. Further analyses produced a reference line (the lowest reference concentration for 50% lethality) showing that the incipient lethality to 50% (i.e., $LC_{50}$) of *C. dubia* occurred at times equal to or greater than 1073 minutes and a monochloramine concentration of 0.018 mg/L. Using application factors, the lower-boundary reference line was shifted to reflect 0% mortality for *C. dubia*. The line was also lowered to account for the species identified in the literature as being more sensitive to inorganic chloramines than *C. dubia*. Using this approach, an incipient Estimated No-Effects Value (ENEV) of 0.0056 mg/L for freshwater organisms was derived for the conservative-level assessment. The same reference line for acute toxicity was adopted to determine a suitable lower boundary line for marine invertebrates due to insufficient acute toxicity data with which to perform reliable modelling with marine and estuarine invertebrates. For the conservative-level assessment, an incipient ENEV of 0.0028 mg/L for marine and estuarine environments was derived by using application factors to reflect 0% mortality and to account for more sensitive species.

A conservative-level assessment of drinking water releases found that even very small direct discharges (e.g., approximately 0.001 $m^3/s$) of chloramine-treated potable water could result in impacts if dilutions are less than 1:10 to 1:100. However, most flows of this nature are indirect and would be subject to chemical demand en route to the surface water; hence, small overland flows would not likely have an impact on aquatic organisms. Larger flows with discharges of greater than 0.01 $m^3/s$, such as from large distribution system leaks, main breaks, fire hose discharge, main flushing, street washing and some industrial and commercial activities, will have a greater possibility of producing impacts. A probabilistic risk assessment for drinking water releases was not conducted because it was not possible to attain the required data (e.g., comprehensive data would be required regarding numbers of major releases, volumes, chloramine concentrations and destinations of flow). In spite of this limitation, severely negative consequences to freshwater ecosystems have occurred in the Lower Mainland of British Columbia, where releases of chloramine-treated potable water due to water main breaks resulted in the mortality of many thousand salmonids and several thousand invertebrates.

Characteristics of chloramine discharges from over 110 WWTPs were screened using a conservative-level assessment. This assessment recommended discharge scenarios for a probabilistic risk assessment. Probabilistic risk assessments were conducted on two wastewater discharges (North Toronto WWTP discharge to the Don River, Toronto, Ontario; Ashbridges Bay WWTP discharge to Ashbridges Bay of Lake Ontario, Toronto, Ontario) and a cooling water discharge (Cloverbar Generating Station discharge to the North Saskatchewan River, Edmonton, Alberta). All discharges were to freshwater rivers and a lake. No marine discharges required probabilistic risk assessment, although there is a potential for negative impact from inorganic chloramine discharge to salt waters.

The probabilistic risk assessment focused on sensitive invertebrate and fish species commonly found in Canada. Sensitive receptors included the freshwater invertebrate, *C. dubia*, and a juvenile freshwater life stage of the anadromous fish, chinook salmon. The chinook salmon was chosen as a fish receptor in spite of the fact that it is not ubiquitous across Canada. However, it is related to other salmonid species, such as rainbow trout (*Oncoryhynchus mykiss*), which together have a widespread presence in Canadian waters. Except for coho salmon (*Oncorhynchus kisutch*), chinook salmon have a sensitivity to chloramines that is similar to or greater than that of other salmonids. Cladocerans (e.g., *C. dubia* and *D. magna*) are representative of other larger and

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smaller invertebrates that together act as food sources for many fish. They form a significant portion of the diet of many fishes, including salmonids, which are themselves an important food, economic and cultural resource for Canadians. To estimate probabilistic risk of chloramines to aquatic biota, each exposure distribution was compared with three incipient lethality endpoints: 50% mortality to *C. dubia* (0.018 mg/L); and 50% (0.112 mg/L) and 20% (0.077 mg/L) mortality to chinook salmon.

In the Don River, forecasted risks were most severe in January, with probabilities of >80% for 50% or greater mortality for *C. dubia* at 1900 m from the source. Lowest risk was forecasted for the month of August, with probabilities of up to 41% for 20% mortality 1900 m from the outfall. For Lake Ontario, there was a probability of >40% for 50% mortality to *C. dubia* in a narrow, semi-elliptical band that was 500 m in width and extended approximately 1000 m. In the North Saskatchewan River, it appeared that elevated risk (i.e., >40% probability of 50% or greater mortality to *C. dubia*) was contained in a plume stretching to a maximum 30 m in width and approximately 3000 m in length.

Since fish are less sensitive than invertebrates to chloramines, risk forecasts for chinook salmon were lower than those for *C. dubia*. Because fish have longer regeneration times, however, the lower probabilities of mortality may lead to longer population consequences for fish than for daphnids. On the other hand, fish are mobile and have the ability to detect and avoid chloramine. Avoidance of chloramine has been reported at 0.05–0.11 mg/L for coho salmon and rainbow trout. The avoidance effects may be offset by conditions in the effluent (e.g., elevated ammonia concentration and elevated water temperatures) that result in attraction. Data were not available to determine whether avoidance and/or attraction can affect the risk forecasts that were determined in this assessment.

**Based on the available data, it is concluded that inorganic chloramines are entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. However, it is concluded that inorganic chloramines are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger to the environment on which life depends. Therefore, inorganic chloramines are considered to be "toxic" as defined in Section 64 of the *Canadian Environmental Protection Act, 1999* (CEPA 1999).**

Risk management efforts should involve limiting the exposure in surface waters from the largest sources (i.e., municipal wastewater facilities, followed by potable and industrial sources). Reducing the exposure of aquatic biota may involve an examination of regional or location-specific characteristics that affect chloramine risk. These would include decay, dilution and the presence of aquatic biota with a sensitivity to inorganic chloramines.

Limiting exposure from unpredictable releases will prove most challenging. Reducing chloramine loading may be technologically feasible for point sources such as waste effluents or cooling waters, but not for geographically and temporally unpredictable releases from drinking water distribution systems. Regional-level control measures, potentially involving changes in treatment procedures, may have to be evaluated for regions with an abundance of aquatic environments that promote chloramine persistence, provide low dilution and contain sensitive aquatic ecosystems. Such measures must not compromise human health protection; selection of options must be based on optimization of treatment to ensure health protection, while minimizing or eliminating potential for harm to environmental organisms.

Although no existing marine or estuarine discharge scenarios were recommended for the probabilistic assessment, new discharges to marine

and estuarine environments could produce negative ecological consequences. The marine environment contains aquatic organisms that are possibly even more sensitive to inorganic chloramines than freshwater species. Therefore, if a facility discharging chloramines to a marine environment is proposed, a precautionary risk assessment is recommended to evaluate site-specific characteristics that affect ecological risk.

# 1.0 INTRODUCTION

The *Canadian Environmental Protection Act, 1999* (CEPA 1999) requires the federal Ministers of the Environment and of Health to prepare and publish a Priority Substances List (PSL) that identifies substances, including chemicals, groups of chemicals, effluents and wastes, that may be harmful to the environment or constitute a danger to human health. The Act also requires both Ministers to assess these substances and determine whether they are "toxic" or capable of becoming "toxic" as defined in Section 64 of the Act, which states:

> ...a substance is toxic if it is entering or may enter the environment in a quantity or concentration or under conditions that
> (a) have or may have an immediate or long-term harmful effect on the environment or its biological diversity;
> (b) constitute or may constitute a danger to the environment on which life depends; or
> (c) constitute or may constitute a danger in Canada to human life or health.

Substances that are assessed as "toxic" as defined in Section 64 may be placed on Schedule I of the Act and considered for possible risk management measures, such as regulations, guidelines, pollution prevention plans or codes of practice to control any aspect of their life cycle, from the research and development stage through manufacture, use, storage, transport and ultimate disposal.

Based on initial screening of readily accessible information, the rationale for the assessment of chloramines provided by the Ministers' Expert Advisory Panel on the Second Priority Substances List (PSL2) (Ministers' Expert Advisory Panel, 1995) was as follows:

> Chloramines — predominantly monochloramine — are found in drinking water, sewers, waste discharges from sewage treatment plants and industrial water supplies treated with chloramines. Other sources include breaks and leaks in watermains, fire fighting runoff and storm-water runoff from domestic water supplies treated with these substances. Chloramines are used as a disinfectant in secondary treatment of drinking water. Chloramines can persist in water from hours to days. They are highly toxic to fish and other aquatic organisms. An assessment is necessary to determine the extent of environmental exposure in Canada and the associated risks.

Based on the conclusion of the Ministers' Expert Advisory Panel that "An assessment is necessary to determine the extent of environmental exposure in Canada and the associated risks," the principal focus of this report is the determination of whether inorganic chloramines are "toxic" under Paragraph 64(a) of CEPA 1999. However, determination of "toxic" to environmental organisms and considerations for subsequent risk management of one of the principal sources of chloramines in the environment — i.e., the disinfection of drinking water supplies — must necessarily be balanced against the beneficial impacts of chloramine use on human health. Monochloramine is used by many water treatment plants (WTPs) in Canada as a secondary disinfectant to maintain residual disinfection activity in potable water distribution systems. In addition, chloramines may be generated as by-products of drinking water chlorination. Chloramination is considered to offer several advantages, such as increased residual activity in the distribution system, reduction of the formation of trihalomethanes (THMs) and other by-products associated with chlorine use, possible control of bacterial biofilm regrowth in the distribution system and, in some circumstances, reduction of taste and odour problems associated with chlorination of drinking water supplies.

Monochloramine is the predominant form of chloramine in chloraminated drinking water, with concentrations far exceeding those of either dichloramine or trichloramine. In 1995, a drinking water guideline of 3.0 mg/L for total chloramines was developed, based on the toxicity of monochloramine (Health Canada, 1995).

Based on a review of recent scientific literature, including 13-week repeated-dose toxicity studies conducted by Health Canada in which rats were administered dichloramine and trichloramine in drinking water (Nakai *et al.*, 2000), significant new information that would impact on the outcome of this previous assessment was not identified (Health Canada, 2000).

In view of the focus of this assessment defined by the Ministers' Expert Advisory Panel and the beneficial impact of the use of chloramine in the disinfection of drinking water supplies, the remainder of this assessment addresses effects on the environment. The only exception is reference in Section 3.4 to the need to ensure adequate health protection while minimizing potential for harm to environmental organisms in considering options for control in relation to drinking water sources.

Although the chemical group chloramines includes both inorganic and organic congeners, the risk assessment was conducted on inorganic chloramines only. This reflects the main intent of the conclusion of the Ministers' Expert Advisory Panel. The rationale for their addition to PSL2 concerned chloramines that are used as disinfectants. The predominant congener used for disinfection is monochloramine, which is an inorganic chloramine species. **Throughout this assessment, the term *chloramine* will refer to *inorganic chloramines* (*monochloramine, dichloramine* or *trichloramine*), unless otherwise specified**. The current state of scientific knowledge relevant to organic chloramines has been researched and documented in a supporting document (see El-Farra *et al.*, 2000). However, where appropriate, other chlorine residual species (both free chlorine and organic chloramine species) are considered, since chloramines are rarely found in an isolated pure form. Further details regarding chloramine chemistry are located in Section 2.1 of this report and in supporting documents no. 1 (Pasternak and Powell, 2000) and no. 2 (El-Farra *et al.*, 2000).

A description of the approaches to assessment of the effects of Priority Substances on the environment is available in a published companion document. The document, entitled "Environmental Assessments of Priority Substances under the *Canadian Environmental Protection Act*. Guidance Manual Version 1.0 — March 1997" (Environment Canada, 1997a), has been published to provide guidance for conducting environmental assessments of Priority Substances in Canada. This document may be purchased from:

Environmental Protection Publications
Environmental Technology
Advancement Directorate
Environment Canada
Ottawa, Ontario
K1A 0H3

It is also available on the Commercial Chemicals Evaluation Branch website at www.ec.gc.ca/cceb1/ese/eng/esehome.htm under the heading "Guidance Manual." It should be noted that the approach outlined therein has evolved to incorporate recent developments in risk assessment methodology, which will be addressed in future releases of the guidance manual for environmental assessments of Priority Substances.

The literature and data search strategies employed in the identification of data relevant to assessment of entry, environmental fate and exposure and potential effects on the environment (prior to January 1999) are presented in Appendix A. Although much of the research on chloramine has been conducted outside Canada, available data on sources, use patterns and fate of chloramines in the Canadian environment have been emphasized. Review articles were consulted where appropriate. However, all original studies that form the basis for determining whether chloramine is "toxic" under CEPA 1999 have been critically evaluated by the staff of Environment Canada and members of an Environmental Resource Group established by Environment Canada to assist in the writing and review of the environmental assessment for chloramines and in the collection of exposure data.

The lead for the PSL assessment of inorganic chloramines was B. Kelso, Environment Canada. This Assessment Report was prepared by J.P. Pasternak, Environment Canada. The supporting documents for the environmental assessment of inorganic chloramines (El-Farra *et al.*, 2000; Farrell and Wan, 2000; McCullum *et al.*, 2000; Pasternak, 2000; Pasternak and Powell, 2000; Moore *et al.*, 2000) were produced by:

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The Environmental Resource Group established by Environment Canada in 1996 to assist in the environmental assessment for chloramines consisted of scientific and technical experts, including:

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A draft of the Assessment Report was made available for a 60-day public comment period (July 8 to September 6, 2000) (Environment Canada and Health Canada, 2000). Following consideration of comments received, the Assessment Report was revised as appropriate. A summary of the comments and responses is available on the Internet at:

www.ec.gc.ca/cceb1/eng/final/index_e.html

The text of the Assessment Report has been structured to address environmental effects relevant to determination of "toxic" under Paragraphs 64(a) and (b).

Copies of this Assessment Report are available upon request from:

Inquiry Centre
Environment Canada
Main Floor, Place Vincent Massey
351 St. Joseph Blvd.
Hull, Quebec
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or on the Internet at:

www.ec.gc.ca/cceb1/eng/final/index_e.html

Unpublished supporting documentation, which presents additional information, is available upon request from:

Commercial Chemicals Evaluation Branch
Environment Canada
14th Floor, Place Vincent Massey
351 St. Joseph Blvd.
Hull, Quebec
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*or*

Environmental Health Centre
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# 2.0 Summary of Information Critical to Assessment of "Toxic" under CEPA 1999

## 2.1 Identity, properties, uses, formation and analytical methods

### *2.1.1 Identity and uses*

Inorganic chloramines consist of three chemicals that are formed when chlorine and ammonia are combined in water: monochloramine, dichloramine and trichloramine. Inorganic chloramines, free chlorine and organic chloramines are chemically related and are easily converted into each other; thus, they are not found in isolation. The chemistry of inorganic chloramines is complex. Site-specific conditions determine the dominant chlorine species that will be formed.

Synonyms for chloramine include chloroamine, combined available chlorine (CAC) and combined residual chlorine (CRC). CRC and CAC include both inorganic and organic chloramines (Kirk-Othmer, 1979).

Organic chloramines, or organochloramines, are a group of perhaps thousands of substances formed via the reaction of free chlorine and inorganic chloramines with various amino acids, peptides or proteins. Although a rigorous evaluation of organic chloramines was beyond the scope of this assessment, the current state of scientific knowledge on organic chloramines is presented in a separate supporting document (see El-Farra *et al.*, 2000).

Total residual chlorine (TRC) includes both CRC and free chlorine. Free chlorine is also called free residual chlorine (FRC) or free available chlorine (FAC), and it includes hypochlorous acid and the hypochlorite ion. Table 1 lists the Chemical Abstracts Service (CAS) registry numbers, molecular formulas and molecular weights for inorganic chloramine and free chlorine compounds.

In the presence of bromide, such as in seawater and some groundwaters, reactive chlorine atoms can be completely or partially replaced by bromine atoms. The collection of reactive chlorine and bromine species is called chlorine-produced oxidants (CPO) or total residual oxidants (TRO).

Inorganic chloramines are formed in wastewaters and cooling waters as a result of a series of reactions that occur when free chlorine is added in the presence of sufficient amounts of aqueous ammonia. The proportion of each residual chlorine species depends on the amount of chlorine added, the conditions present in the water/influent as well as the chlorine contact time.

In potable water, inorganic chloramines (predominantly monochloramine) are

**Table 1** Chemical description of combined and free chlorine congeners

| Item | Inorganic chloramine compounds | | | Free chlorine compounds | |
|---|---|---|---|---|---|
| | Monochloramine | Dichloramine | Trichloramine | Hypochlorous acid | Hypochlorite ion |
| CAS No. | 10599-90-3 | 3400-09-0 | 10025-85-1 | 7790-92-3 | – |
| Molecular formula | $NH_2Cl$ | $NHCl_2$ | $NCl_3$ | HOCl | OCl |
| Molecular weight | 51.48 | 85.92 | 120.37 | 52.46 | 51.45 |

intentionally produced, usually as a secondary disinfectant, for several reasons, including:

- persistence and the ability to maintain a chlorine residual or disinfection capability throughout the distribution system, thereby eliminating costs for water supply services associated with the need for chlorine booster stations;
- adequate disinfection capability for the protection of humans from pathogenic and other microorganisms;
- ability to penetrate and prevent biofilm accumulation in municipal distribution systems;
- lower tendency to form trihalomethanes (THMs) and other disinfection by-products in comparison with free chlorine; and
- minimization of objectionable tastes and odours (AWWARF, 1993).

Chlorination is also used to disinfect wastewater. Disinfection involves the oxidation of reactive organic material and the reduction or elimination of bacteria, viruses and protozoa by the chlorine residual. Consideration of disinfection efficiency, ease of application and cost has led to the use of chlorine as a primary disinfectant in food processing, seafood production and municipal wastewater treatment.

Chlorine and chloramine are used as biocides to reduce biofouling in water cooling towers and cooling systems of electrical generating stations, as well as at desalination, petrochemical, paint and metal fabricating facilities. Chlorination is also used as a treatment to remove slime and algae, bacteria and their extracellular excretions or to eliminate hydroids, barnacles, mussels, clams and oysters at water intakes for electrical generating facilities (Coulston *et al.*, 1994).

### *2.1.2 Chemistry of chloramine formation*

A variety of physical and chemical properties for chlorine species are presented in Table 2.

The formation of inorganic chloramines is adequately described using reactions involving aqueous chlorine and ammonia. In general, the reactions are governed by two main parameters: pH and the ratio of chlorine to ammonia. Time of reaction and temperature are also factors in these reactions. A thorough review of inorganic chloramine formation is presented in the supporting document prepared by El-Farra *et al.* (2000). Salient features of chloramine chemistry are presented below.

In aqueous solution, chlorine ($Cl_2$) is present as either hypochlorous acid (HOCl) or hypochlorite ion ($OCl^-$), although it is still usually referred to as chlorine. Similarly, ammonia ($NH_3$) may also be present as the ammonium ion ($NH_4^+$) but is usually referred to as ammonia. The relative amounts of each of these species are determined by the pH of the water and the ionization constants for chlorine and ammonia ($pK_{a,HOCl} = 7.54$; $pK_{a,NH_3} = 9.3$; Snoeyink and Jenkins, 1980). The result of the reaction of these species is the formation of chlorinated species of ammonia: monochloramine ($NH_2Cl$), dichloramine ($NHCl_2$) and trichloramine ($NCl_3$) (White, 1992).

Simplified reactions are often used to illustrate the complex effect of the chlorine-to-ammonia ratio on inorganic chloramine formation:

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O$$
$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$$
$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$$

In looking at the reactions from left to right (the forward reactions), as the ratio of chlorine (hypochlorous acid) to ammonia increases, greater chlorine substitution is observed. These are equilibrium reactions, with the two arrows indicating that both forward and reverse reactions occur to an appreciable extent. Thus, there will always be at least small amounts of the materials shown on both sides of each equation present in solution. Also, the reverse reactions indicate that if chloramines are added to water, certain amounts of free chlorine and

**TABLE 2** Physical and chemical properties of combined and free chlorine congeners[1]

| Parameter | $NH_2Cl$ | $NHCl_2$ | $NCl_3$ | HOCl | $Cl_2$ |
|---|---|---|---|---|---|
| Physical state at STP | Liquid | Liquid | Liquid | Liquid | Gas |
| Colour | Colourless | n/a | Bright yellow | Green-yellow | Yellow-green |
| Boiling point (°C) | n/a[2] | n/a | 70 | n/a | –34.05 |
| Melting point (°C) | –66 | n/a | –40 | n/a | –100.98 |
| Water solubility | Soluble | Soluble | Limited to hydrophobic | 7290 mg/L | Slightly soluble (1% at 9.6°C) |
| pK | 14 ± 2[3] | 7 ± 3 | n/a | 7.40–7.54 | n/a |
| Henry's law constant ($Pa \cdot m^3/mol$) | 557 ± 61 at 20°C[4] | n/a | Very volatile[5] | n/a | n/a |
| Other comments | May explode at room temperature; most stable in aqueous solution | Pungent odour | Powerful, irritating odour, highly explosive, extremely hydrophobic | Stable only in aqueous solution | Pungent odour |

[1] Sources: Jolley, 1956; Kirk-Othmer, 1979; Snoeyink and Jenkins, 1980; Hand and Margerum, 1983; Reckhow *et al.*, 1990; Lorberau, 1993; Lide, 1998.

[2] Data or information not available.

[3] Estimated based on pK of other chlorine residuals.

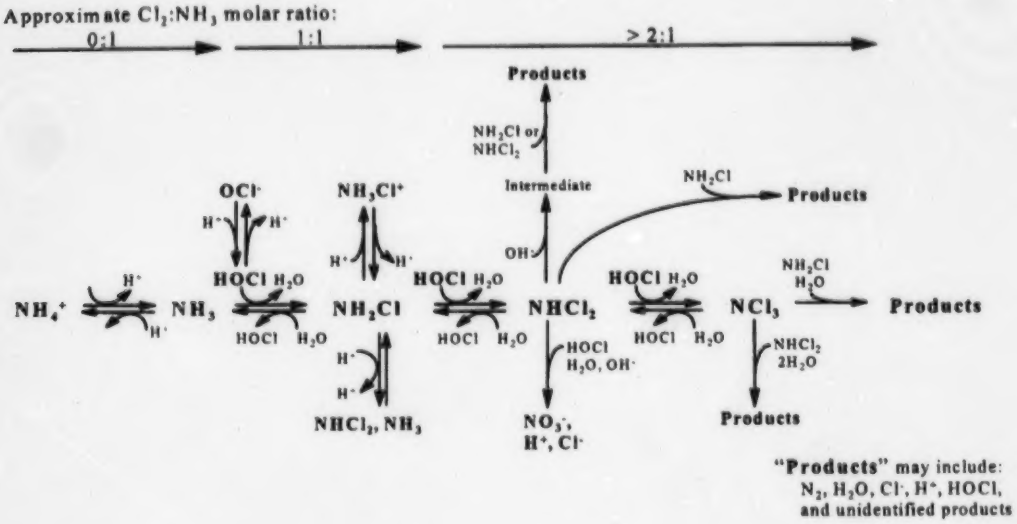
[4] Monochloramine was the dominant and usually the only species detected using the DPD ferrous titrimetric method of analysis. Air/water partition coefficient ($K_{aw}$) = 0.24 ± 0.03.

[5] Henry's law constant not available. Vapour pressure is 19.998 kPa at 20°C.

different chloramines or ammonia will be generated. These reverse reactions are called hydrolysis reactions because water is involved.

In reality, chloramine chemistry entails a complex series of reactions involving the species and pathways identified in Figures 1 and 2. At hypochlorous acid-to-ammonia molar ratios of greater than approximately 1.5:1 to 2:1, oxidation reactions occur in addition to substitution reactions, with the net result being a decrease in the concentrations of chloramine species present. For the relatively neutral to slightly basic conditions encountered in most aquatic receiving environments, monochloramine and/or dichloramine are generally the chloramine species detected in greatest concentration. At pH values above 8 and hypochlorous acid-to-ammonia molar ratios of 1:1 or below, monochloramine is the only observed chloramine. Dichloramine and trichloramine are formed at higher molar ratios and at lower pH values. In slightly acidic water or when the hypochlorous acid-to-ammonia molar ratio is greater than 1:1, dichloramine may account for the largest fraction of the total chlorine concentration. However, trichloramine is the only chloramine observed below pH 3. Trichloramine proportions diminish up to pH 7.5 at hypochlorous acid-to-ammonia ratios greater than 2:1. Above pH 7.5, trichloramine is not detectable at any hypochlorous acid-to-ammonia ratio.

**FIGURE 1** Summary of ammonia/chlorine reactions (adapted from Jafvert and Valentine, 1992)




Certain wastewaters and cooling waters are "breakpoint-chlorinated" prior to discharge, which results in a discharge with low ammonia and residual chlorine concentrations. Under optimal conditions, the ammonia is completely oxidized to nitrogen gas ($N_2$), and the chlorine is reduced to chloride ion ($Cl^-$). The breakpoint phenomenon occurs quickly (within a few minutes) and to a significant extent in the pH range 6–9, the pH range for most natural waters (see Figure 3). It is generally described as a relationship between the ratio of chlorine to ammonia applied and the resulting TRC concentration (see Snoeyink and Jenkins, 1980; Montgomery, 1985; Metcalf and Eddy, Inc., 1991; Stumm and Morgan, 1996).

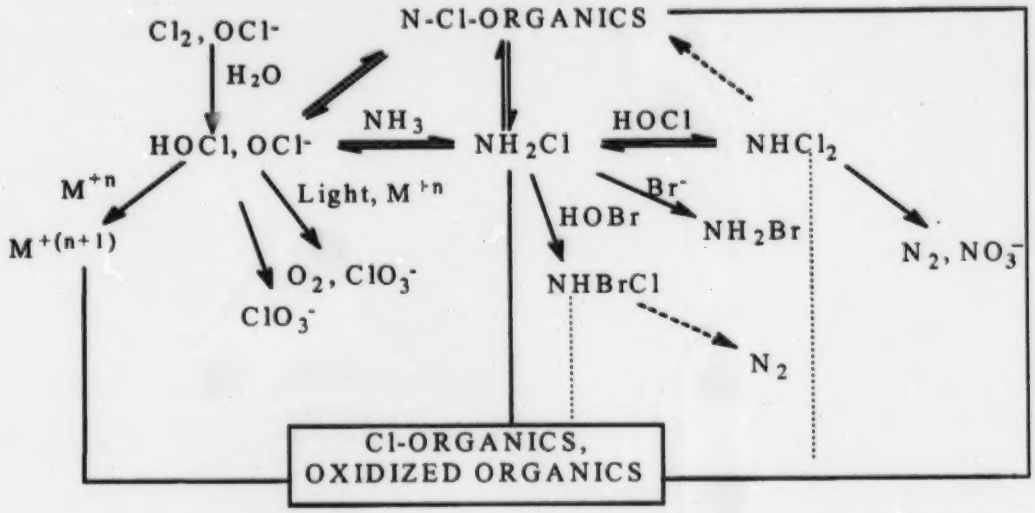
Figure 3 shows that increases in both the monochloramine concentration and combined chlorine residual occur for increases in the chlorine-to-ammonia molar ratio from 0:1 up to a maximum at approximately 1:1. It is generally thought that this is the region of the breakpoint curve that most often represents the mix of chlorine and ammonia in chlorinated receiving waters, making monochloramine the chloramine species expected to be in highest concentration.

The presence of certain organic amino compounds complicates the breakpoint process by providing an additional source of chlorine demand and by reacting with the added chlorine to form relatively stable organochloramines that cannot be completely oxidized. Organochloramine species form simultaneously with the inorganic chloramines. This results in a breakpoint that is not as sharp as that observed when reacting ammonia and free chlorine in isolation. Due to the higher chlorine demand, the breakpoint may be shifted to a chlorine-to-nitrogen molar ratio that is higher than 1.65:1 (see El-Farra *et al.*, 2000).

### *2.1.3 Analytical methods*

Concentrations of inorganic chloramines in aqueous solution may decrease very rapidly upon sampling. As a result, care must be taken to minimize chemical losses due to photolysis, volatilization and contamination. If storage is necessary, samples should be maintained at 4°C for no longer than 1 week (Environment Canada, 1999a). APHA *et al.* (1995) recommend that analysis for residual chlorine compounds be conducted immediately after sampling.

**FIGURE 2** Principal chemical pathways for the reaction, degradation and fate of free chlorine in aquatic environments (adapted from Jolley and Carpenter, 1983)



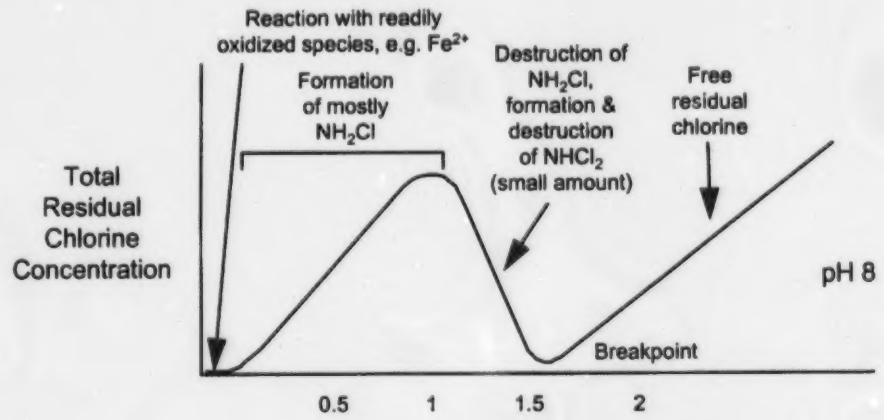

Several analytical methods are used to determine the available chlorine in solution (Jolley and Carpenter, 1983). For CRC, the commonly used methods include N,N-diethyl-p-phenylenediamine (DPD) colorimetry, DPD titration and amperometric titration (Fava and Seegert, 1983; APHA *et al.*, 1995; Harp, 1995).

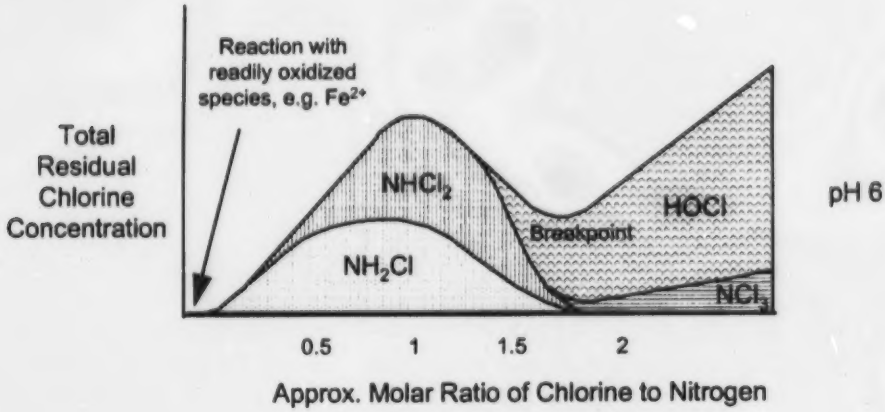
The DPD colorimetric and the DPD titration methods are based on the same chemistry, and, for most samples, there are no clear advantages to the use of either method. The DPD colorimetric method is, however, faster and easier to operate. On the other hand, it is prone to interferences from sample colour and turbidity, while the DPD titration method does not suffer from these interferences.

The DPD methods can be used to estimate the separate monochloramine, dichloramine and combined fractions for natural and treated waters. Both methods are based on the total oxidizing capacity of the sample being analyzed; thus, both are readily subject to interferences from other oxidizing agents, such as chlorine dioxide, hydrogen peroxide, bromine and ozone. They cannot be used with marine water and some groundwaters where significant quantities of bromine will be present (Harp, 1995). Under ideal conditions, the DPD colorimetric method has a minimum detection limit of 0.01 mg/L as $Cl_2$, while the DPD titration method has a minimum detection limit of 0.018 mg/L as $Cl_2$ (APHA *et al.*, 1995).

Amperometric titration requires a higher degree of skill and care than both the DPD methods. It can be used to determine TRC and can differentiate between FRC and CRC; however, several factors may affect the determination of chlorine species. Metallic ions of silver, copper and iron have been reported as interferences or may diminish the electrode response. Oily or foamy surfactants may adhere to the electrodes, reducing their sensitivity. The violent stirring of some titrators may lower chlorine concentrations by volatilization. Also, oxidized forms of manganese may produce a falsely higher concentration of dichloramine (Harp, 1995). Interference can also occur in highly coloured waters. If present, various organic chloramines can be measured by amperometric titration as free chlorine, monochloramine or dichloramine, depending

**FIGURE 3** Graphic representation of the ideal breakpoint phenomenon for the chlorination of ammonia at pH 6 and 8 (El-Farra *et al.*, 2000)




on the activity of chlorine in the organic compound. As with the DPD methods, amperometric titration cannot distinguish inorganic chloramines from organic chloramines (APHA *et al.*, 1995). The minimum detection limit of amperometric titration is approximately 0.01 mg/L as $Cl_2$ under ideal conditions.

High-pressure liquid chromatography (HPLC) with post-column electrochemical detection can be used to quantify inorganic chloramines in potable water, surface (fresh) water, groundwater, and industrial or municipal wastewater. Unlike the previously discussed methods, the HPLC method is not subject to interference from organic chloramines; however, its use requires a skilled analyst, and the instrumentation is substantially more expensive than that used in the traditional methods. HPLC provides an inherently mild condition (neutral pH) and employs direct analysis without sample alteration for detecting inorganic chloramines. This method can be used to calculate total organic chloramines in conjunction with the DPD ferrous ammonium sulfate (FAS) titration method (i.e., analysis of TRC and FRC by DPD FAS titration

method, analysis of inorganic chloramines by HPLC: total organic chloramines = TRC – FRC – monochloramine – dichloramine). The HPLC method is currently unable to differentiate combined chlorine species from combined bromine species in marine and estuarine waters. This HPLC method has a detection limit of 0.01 mg/L as $Cl_2$ (Environment Canada, 1999a).

## 2.2 Entry characterization

Chloramines are released to the Canadian environment mainly by municipal and industrial sources in potable water, effluents and cooling water. To quantify releases of chloramine into the Canadian environment, surveys were sent to municipalities and industries across Canada (Environment Canada, 1997b,c,d). Surveys were sent to all Canadian municipalities with populations exceeding 5000 (based on the 1994 Census) to determine chloramine production and release to the Canadian environment from chlorinating wastewater treatment facilities (which do not dechlorinate before discharge), as well as from drinking water treatment facilities and distribution systems (Environment Canada, 1997b,c). As per its request, Quebec was excluded from the municipal survey. The Municipal Water Use Database (MUD) (Environment Canada, 1996) was consulted to determine which municipalities in Quebec used chloramines as a secondary disinfectant for potable water and to obtain additional data with which to estimate loading from this province.

Most respondents reported concentrations as TRC, since the analytical methods used were not capable of differentiating between inorganic and organic chloramines. For chloraminated drinking water, the TRC concentration will be almost completely due to monochloramine. Effluent TRC will be predominantly composed of inorganic and organic chloramines in proportions dependent on site-specific conditions.

A survey was administered to industries across Canada that may be discharging chlorinated effluents or cooling waters under Section 16 of the *Canadian Environmental Protection Act* (CEPA). Industries were required to respond if their facility produced or released a trigger quantity of 1000 kg of chloramines per year (Environment Canada, 1997c).

### *2.2.1 Municipal potable water*

The inventory of chloramines produced and released to the environment from potable water included chloramines intentionally formed for disinfection purposes. Potable water treated with free chlorine may also contain inorganic and organic chloramine species, depending on the concentrations of ammonia and organic nitrogen present at the time of chlorination. This latter source has not been considered in this source inventory. However, it is recognized that the assessment of fate and effects as described in this Assessment Report would also relate to releases of inorganic chloramines resulting from potable water treated with free chlorine.

In 1996, 64 Canadian municipalities with populations exceeding 5000 used potable water that was intentionally treated with chloramine. There were 29 facilities in Canada treating a total of approximately 1 220 000 000 $m^3$ of drinking water per day, which serviced approximately 6.9 million Canadians in 1996. In 1995, there were 28 facilities that treated an approximate total of 1 200 000 000 $m^3$/day. The survey revealed that some of Canada's most populated regions produce and/or use chloramine-treated drinking water. These included the Greater Toronto Area, Edmonton, the Regional Municipalities of Ottawa-Carleton, Hamilton-Wentworth and Peel, and the Capital Regional District of Victoria.

The largest producer of chloramines in potable water during 1996 was Ontario (67.7%), followed by Alberta (23.1%), Saskatchewan (4.9%) and British Columbia (2.9%). Newfoundland and Quebec produced substantially less (approximately 1.5%). Nationally, drinking water treatment facilities achieve chloramine concentrations of between

0.01 and 4.80 mg/L at the source and throughout the distribution system. The average chloramine concentration in drinking water (at the source and throughout the distribution system) was approximately 1.0 mg/L in 1995 and 1996. The average minimum concentrations were 0.61 mg/L and 0.60 mg/L in 1995 and 1996, respectively, whereas the average maximum concentrations were 1.66 mg/L and 1.46 mg/L in the same years. The national average, average minimum and average maximum chloramine concentrations in potable water refer to the flow-weighted arithmetic mean of all average, minimum and maximum chloramine or TRC concentrations reported from all surveys (Environment Canada, 1997b).

Of the 213 respondents to the drinking water survey, approximately 24% were able to provide some data regarding environmental releases. Accidental drinking water releases are typically episodic and unpredictable with respect to their time, duration and location and occur from main breaks, leaks and overflows from treatment facility reservoirs. Most distribution main leaks and breaks have discharges of less than 0.01 $m^3/s$ and durations of less than 8 hours. However, releases of up to approximately 1.0 $m^3/s$ and lasting several days or weeks have occurred. An estimated 9% of the total volume of water treated was released accidentally to the environment in 1996.

Outdoor uses (e.g., for lawn/garden watering, driveway washing and car washing) accounted for an estimated 7.5% and 7% of the total volume of chloramine-treated drinking water in 1995 and 1996, respectively. Lesser releases of chloraminated drinking water also occur from fire fighting, street cleaning and main flushing.

Of the 15 facilities that were contacted for data characterizing chloramine-containing waste streams from municipal drinking water treatment plants, 10 facilities dechlorinated their waste streams, diverted them to sanitary sewers or did not discharge any waste streams at all. The remainder discharged directly to a freshwater environment. Based on the available data, WTP backwash wastes accounted for an estimated 22 100 000 $m^3$ and a total TRC loading of approximately 8230 kg in 1997. Unlike typical effluents, these discharges are intermittent, lasting approximately 15–30 minutes per discharge and occurring up to approximately 6 times per day. Reported CRC concentrations in waste ranged from approximately 0.07 to 2.00 mg/L (approximate flow-weighted mean = 0.370 mg/L).

### 2.2.2 *Municipal wastewater*

The Environment Canada (1997c) municipal wastewater survey had an overall 49% response rate and a 61% response rate of municipalities that chlorinated their wastewater. To fill the remaining data gaps, various other sources were consulted to determine the loading of chlorinated wastewater to the Canadian environment (e.g., Environment Canada, 1996; OMEE, 1997; Alberta Environmental Protection, 1998). It was determined that 173 municipal wastewater treatment plants (WWTPs) disinfected their wastewater with chlorine and did not dechlorinate prior to discharging to aquatic systems in 1996. Dechloronation involves the removal of residual chlorine usually by physical or chemical processes. Many WWTPs dechlorinate effluents at all times when they chlorinated for disinfection purposes (e.g., all WWTPs in the Greater Vancouver Regional District).

TRC concentrations ranged between the detection limit (usually 0.01 mg/L) and 4.00 mg/L for 1995 and 1996. The national average TRC concentrations in chlorinated municipal effluent were 0.72 mg/L and 0.70 mg/L for 1995 and 1996, respectively. The national average maximum TRC concentrations were 1.45 mg/L and 1.36 mg/L for 1995 and 1996, respectively. Total discharges of chlorinated municipal wastewater effluent were approximately 1 770 000 000 $m^3$ and 1 830 000 000 $m^3$ for 1995 and 1996, respectively. The total average loading of TRC to surface water from municipal sewage treatment effluent was approximately 1 300 000 kg in both 1995 and 1996.

Based on the average TRC loading reported by municipalities in 1996, Ontario produced most of Canada's chlorinated municipal sewage treatment plant effluent (89.9%), followed by Saskatchewan (4.1%), Alberta (2.0%) and Nova Scotia (1.1%). The remaining provinces each produced less than 1% of the national chlorinated wastewater discharged. Production of chlorinated sewage was proportionally similar in 1995. The Yukon and Northwest Territories did not discharge any chlorinated wastewater effluent in 1996.

In 1996, approximately 98% of TRC loading was to a freshwater environment (23% to a river, 48% to a lake, 27% to an unspecified freshwater type) and 2% to a marine/estuarine environment. All marine discharges of chlorinated municipal wastewater occurred in Atlantic Canada.

### *2.2.3 Industrial effluents and cooling waters*

In total, 54 facilities responded to the industrial survey (Environment Canada, 1997d).

#### 2.2.3.1 Cooling waters

According to the industrial survey responses, 21 facilities in Canada used chlorine to treat cooling water and did not dechlorinate prior to discharge in 1995 and 1996. Many of these facilities were petroleum refineries (6 facilities in total), metal fabricators (4), chemical manufacturers (4) and electrical generating stations (2). In addition to the survey, all major electrical utilities, with the exception of Hydro-Québec, were contacted for detailed information regarding chlorination of cooling waters. It was found that EPCOR and Kirkland Lake Power Corporation each operated a generating station that produced or released chlorine or chloramine over the trigger quantity of 1000 kg per year in 1995 and/or 1996. Total discharge of chlorinated cooling water in Canada for 1996 was approximately 132 000 000 $m^3$, and the total TRC loading was approximately 86 000 kg. The national average TRC concentration in cooling water was 0.77 mg/L for 1996 (range = 0.46–1.48 mg/L). In 1996, the largest proportion of discharged chlorinated cooling water was found in Alberta (TRC loading was approximately 33 400 kg), Quebec (26 400 kg) and Ontario (25 000 kg).

#### 2.2.3.2 Zebra mussel control

In Ontario and Quebec, chlorine is used to inhibit the fouling of intake and outfall pipes by zebra mussels. Chlorination to control zebra mussel populations is required only between June and October, and then only when the plants are in operation (Environment Canada, 1993).

Ontario Hydro's Nuclear Division used chlorine to control zebra mussel fouling at their nuclear generation stations on the Great Lakes (Bruce, Darlington and Pickering). One facility in Quebec chlorinated discharge for zebra mussel control in 1995 and 1996. The average combined flow for all stations was approximately 6 350 000 000 $m^3$/d. The average TRC concentration for 1996 was approximately 0.01 mg/L. The total TRC loading from all facilities was approximately 142 000 kg in 1996.

#### 2.2.3.3 Industrial wastewater

The chemical composition of industrial wastewater varies widely depending on the nature of the industry. In contrast to the relatively consistent characteristics of domestic sewage, industrial wastewater often has quite different characteristics, even for similar industries. Industrial wastewater can include employees' sanitary wastes, process wastes from manufacturing, wash waters, and water from heating or cooling operations (Henry and Heinke, 1996). Of the industrial surveys received, 18 facilities were found to discharge a total of 22 800 000 $m^3$ of chlorinated wastewater in 1996. The total TRC loading from industrial wastewater in 1996 was approximately 4900 kg. The average TRC concentration for these facilities is 2.1 mg/L, with concentrations ranging between undetectable and 3.6 mg/L for 1995 and 1996.

Five facilities in Ontario discharge chlorinated wastewater on a continuous basis. Detailed information regarding these sites was

not available. The province of Newfoundland has one industry that discharges chlorinated wastewater at an approximate rate of 655 000 $m^3/d$. This facility's wastewater has an average TRC concentration of 1.0 mg/L, with concentrations ranging between 0.8 and 1.2 mg/L.

### *2.2.4 Summary*

The source inventory found that most of the chloramine/TRC loading from all known sources occurred in Ontario (approximately 80% of total), followed by Quebec (8%) and Alberta (6%) (Table 3). As shown in Figure 4, approximately 99% of all chloramine and TRC discharges are to fresh water, and only approximately 1% are destined for a marine environment. Discharges to land amounted to 0.01% of all emissions. This release was too small to be shown in Figure 4. Since there are no comprehensive data available for the destination of potable water flows from distribution systems, these data have not been included in Figure 4.

## 2.3 Exposure characterization

### *2.3.1 Environmental fate*

All releases of chloramine compounds into the Canadian environment reported by the municipal and industrial surveys (Environment Canada, 1997b,c,d) were in aqueous solution. Hence, chloramine fate is governed largely by water-phase processes. However, other phases, such as air and soils, are also involved.

#### 2.3.1.1 Air

Studies describing the fate of chloramines in ambient air do not exist. In the air phase, it would be expected that chloramines would dissipate due to advection and dilution and would be subject to reaction, although no information has been located characterizing reactions for chloramines in a gaseous state. Various studies indicate that chloramines are thermodynamically unstable and susceptible to photolysis (Gilbert *et al.*, 1987; Gilbert and Smith, 1991; Lorberau, 1993). Monochloramine and dichloramine are very water soluble and are thus susceptible to removal from the atmosphere by rain. Gas-phase trichloramine is explosive in nature, particularly in the presence of monochloramine and dichloramine or when *in vacuo*. This has had an inhibiting effect on relevant scientific research (Gilbert *et al.*, 1987).

#### 2.3.1.2 Water

Chloramine and FRC species are easily transformed to one another in water, and various CRC and FRC species are usually present simultaneously. If FRC is released to a fresh surface water, inorganic or organic chloramines may be formed immediately, and the dominant inorganic chloramine species will be based on relevant site-specific conditions, particularly the pH and molar ratio of hypochlorous acid to ammonia. Conditions prevalent in natural fresh surface waters are conducive to the formation and presence of monochloramine and dichloramine (see Section 2.1.1). Monochloramine is, however, the principal inorganic chloramine in fresh waters due to its rapid formation and relative stability in comparison with other CRC and FRC species (Johnson, 1978; Margerum *et al.*, 1978). Trichloramine is rarely found in the environment, since its formation is dependent on uncommon natural conditions (i.e., pH <4.4; hypochlorous acid-to-ammonia ratio >7.6:1). Once formed, trichloramine is extremely volatile (Table 2) and will move quickly to the air phase.

The addition of FRC or CRC to water containing bromine will lead to the formation of bromamines. This is particularly an issue in seawater; however, some groundwater and fresh surface water also have sufficient amounts of bromine to produce bromamines (see El-Farra *et al.*, 2000). Inorganic chloramines are thus viewed as being in dynamic equilibrium with several forms of residual oxidants. Since studies describing the fate of inorganic chloramines are few, and because most researchers describe the fate of TRC with little or no speciation, the

**TABLE 3** Estimated chloramine and TRC loading to the Canadian environment from all sources in 1996[1]

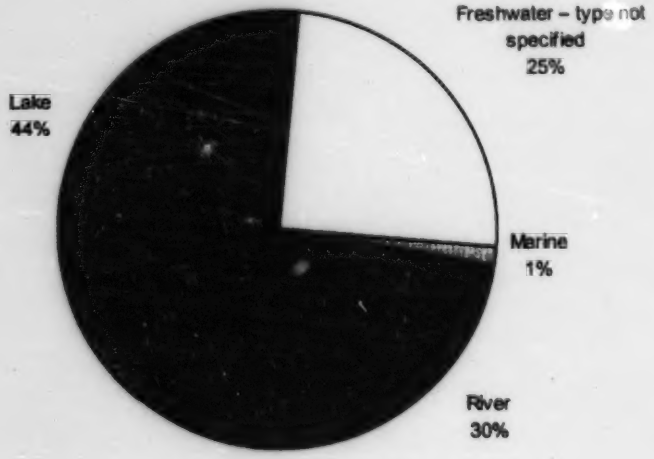
| Province | Chloramine (kg) from drinking water releases[2] | TRC (kg) from municipal wastewater | TRC (kg) from cooling water | TRC (kg) from zebra mussel control | TRC (kg) from industrial wastewater | Total TRC (kg) | Proportion of total (%) |
|---|---|---|---|---|---|---|---|
| British Columbia | 3 200 | 11 800 | – | – | – | 15 000 | 0.84 |
| Alberta | 39 200 | 26 600 | 33 400 | – | – | 99 200 | 5.55 |
| Saskatchewan | 10 200 | 53 300 | 950 | – | – | 64 450 | 3.61 |
| Manitoba | – | 5 350 | – | – | 120 | 5 470 | 0.31 |
| Ontario | 196 000 | 1 170 000 | 25 000 | 33 800 | 444 | 1 425 244 | 79.80 |
| Quebec | 2 480 | 5 660 | 26 400 | 108 000 | – | 142 540 | 7.98 |
| Newfoundland | 1 250 | 1 210 | – | – | 695 | 3 155 | 0.18 |
| New Brunswick | – | 11 200 | – | – | – | 11 200 | 0.63 |
| Prince Edward Island | – | 1 730 | – | – | – | 1 730 | 0.10 |
| Nova Scotia | – | 14 300 | – | – | – | 14 300 | 0.80 |
| **National total** | **252 330** | **1 301 150** | **85 830**[3] | **141 800** | **4 909**[3] | **1 786 019** | **100.00** |

[1] Source: Environment Canada (1997b,c,d).

[2] Drinking water releases include accidental losses, outdoor uses, street cleaning, fire fighting, construction activities, water main flushing, filter backwash and other waste discharges from WTPs.

[3] Totals include confidential data not identified in provincial totals.

**FIGURE 4** Chloramine and TRC loading from chlorinated cooling water and municipal and industrial effluent (Environment Canada, 1997a,b,c)



analysis of chloramine fate has involved an examination of the behaviour of TRC to infer the behaviour of chloramines.

Inorganic chloramine fate is governed largely by water-phase processes, including dilution, mixing, advection, chemical demand (reactions with organic and inorganic compounds), benthic demand, photodegradation, volatilization, sediment adsorption and reaction, and sediment-associated transport, deposition, burial and resuspension.

Mixing and dispersion of discharges containing chloramines depend on water body morphometry, as well as the magnitude and direction of water flows and currents. If the dilution of the effluent is small and/or if the current velocity is fast, complete mixing may not occur for several kilometres downstream from the source (e.g., Milne, 1991). The effluent may then be contained in a long narrow plume. For instance, discharges from the E.L. Smith and Rossdale WTPs to the North Saskatchewan River in Edmonton, Alberta, did not completely mix with the river, and significant transverse concentration gradients existed in a plume for considerable distances downstream (Milne, 1991). TRC concentrations measured in the Rossdale WTP waste discharge ranged from 2.05 to 2.16 mg/L; at 1402 m from the source, TRC concentrations ranged from <0.01 (detection limit) to 0.065 mg/L (Milne, 1991). A discussion of mixing, advection and dispersion in rivers, lakes, and estuarine and marine environments has been provided with reference to dispersion modelling in a supporting document entitled "Tier 2 Exposure Assessment of Effluents for Inorganic Chloramines" (McCullum *et al.*, 2000).

Decay rate constants (k) of inorganic chloramines are highly variable, varying by 4 orders of magnitude depending on the type of water used (e.g., fresh or salt water, pH, surface or deionized water, etc.), chlorine/chloramine dose, study design (e.g., *in situ* versus laboratory) and experimental conditions. Generally, studies conducted under controlled laboratory conditions produce decay rates that are at least 1 order of magnitude lower than those produced in *in situ* studies (Milne, 1991). This is likely due to the use of controls that limit many environmental decay processes, such as volatilization, photodegradation and benthic demand.

Water column chloramine demand is produced by chemical reactions with inorganic (e.g., $I^-$, $S^{2-}$, $Fe^{2+}$, $Mn^{2+}$, $HSO_3^-$ and $NO_2^-$ ions) and organic (e.g., alkyl sulfides, amines and some nitrogen heterocyclic aromatics) substances, as well as adsorption to solids and colloidal matter (Morris and Isaac, 1980; Christman *et al.*, 1983; Scully and White, 1992). Reactions in aquatic environments are affected by temperature, pH and turbulence (Heinemann *et al.*, 1983; Abdel-Gawad and Bewtra, 1988; Milne, 1991).

Under controlled conditions (no sunlight or volatilization, 15°C) using deionized water mixed with various fresh surface waters (Norrish Creek, British Columbia; North Saskatchewan River, Alberta; and Grand River, Ontario), Environment Canada (1998a) determined decay rate constants ranging from approximately 0.017 to 0.413 per day (half-life of 1.67–40.8 days) for monochloramine. Using deionized water and seawater mixtures from Burrard Inlet, British Columbia, Environment Canada (1998b) determined monochloramine decay rate constants of 0.74–1.01 per day (half-life of 0.68–0.94 days). Abdel-Gawad and Bewtra (1988) determined a TRC decay rate constant of 0.48 per day (half-life of 1.44 days) using municipal wastewater–St. Claire River water mixtures at 20°C. Heinemann *et al.* (1983) determined chemical demand rate constants of 1.73–23.76 per day (half-life of 0.03–0.40 days) at 20°C also using effluent–surface water mixtures.

Lee *et al.* (1982) and Heinemann *et al.* (1983) indicated that TRC is very volatile and accounted for 20–80% of the lost chlorine from various Colorado rivers. There are no volatilization rate constants derived specifically for chloramines. TRC may be influenced

by photodegradation; however, when all environmental decay processes are combined, its effect may be nullified (Milne, 1991).

The overall or gross decay rate incorporates different environmental factors, which, when taken together, may represent natural environmental conditions. A focussed review of the literature revealed that the first and third quartiles of reported overall decay rate constants for CRC, TRC and TRO were approximately 0.70 and 20.0 per day (half-life of 0.03–1.0 days), respectively (see Pasternak, 2000). Reckhow *et al.* (1990) derived higher rates of *in situ* monochloramine decay (i.e., 144 per day; half-life of 0.005 days). Wisz *et al.* (1978) undertook an evaluation of CRC decay from chlorinated municipal wastewater discharged to Aurora Creek (now called Tannery Creek), Ontario, and reported that monochloramine decay rate constants ranged from 4.97 per day in the winter to 19.54 per day in the summer (half-life of 0.04–0.14 days).

#### 2.3.1.3 Sediment

Inorganic chloramine loss from the water column may occur via adsorption and reaction with suspended solids and bottom sediments (Milne, 1991). Environment Canada (1998b) found that sediments at a concentration of 5000 mg dry weight/L from the Grand River, North Saskatchewan River and Downes Creek produced monochloramine decay rate constants of 0.50, 0.28 and 14.83 per day (half-lives of 1.4, 2.5 and 0.05 days), respectively. The highest decay rates were associated with sediments that had higher organic nitrogen and carbon and that were suspected to contain biologically active materials (i.e., stream scum).

Stream beds may be covered with active biological materials in the form of slimes, sludges and algae, particularly at wastewater outfalls. This biological material has a capacity for uptake of residual chlorine (Krenkel and Novotny, 1980). The rate of pollutant uptake in this layer (or the rate produced by benthic demand) will be influenced by the type of biological material, temperature, flow and sediment characteristics and depth (Milne, 1991). Due to its dependence on site-specific conditions, it is very difficult to make generalizations regarding chloramine loss rate due to benthic demand, except that it may be extremely rapid.

One study provided a preliminary estimate of benthic demand on TRC. Milne (1991) undertook *in situ* benthic demand tests in the North Saskatchewan River, just upstream of the E.L. Smith Water Treatment Plant, Edmonton, Alberta, in September and October of 1990 and September of 1991. He observed a TRC loss rate constant (geometric mean) of 448–591 per day (half-life of 0.001–0.002 days). Benthic demand was in fact higher than the overall measured TRC decay rate constants for the North Saskatchewan River (i.e., 20.0 and 28.0 per day, or half-life of 0.03 and 0.04 days). It is unknown whether prior exposure to residual chlorine would affect benthic uptake of chloramine or whether adsorption or reaction was occurring, although the latter seems apparent given the organic nature of the benthic material.

#### 2.3.1.4 Soils

There are no studies evaluating the fate of inorganic chloramines on/in soils. Based on related information on fate associated with sediments and surface waters, inorganic chloramines would experience chemical reaction with particulates, volatilization and photolysis at the soil surface and chemical reaction and adsorption within the soil matrix. Inorganic chloramine may oxidize surface layer soil organic matter (Bodek *et al.*, 1988), particularly materials composed of organic nitrogen compounds, such as alkyl sulfides, amines and some nitrogen heterocyclic aromatics (e.g., see Christman *et al.*, 1983; Scully and White, 1992). Zellmer *et al.* (1987) speculated that the components of a fine-silty clay loam soil had completely bound or inactivated sodium hypochlorite in the C-8 mixture (15% perchloroethylene, 8% calcium hypochlorite, 1% emulsifier and 76% water). They simulated spill conditions and found no

residual chlorine concentrations at any depth of a 68-cm soil core after 144 hours using the starch-iodine method of analysis.

#### 2.3.1.5 Biota

Accumulation of inorganic chloramine in biota is not likely, since inorganic chloramines are known to be transient and highly reactive with organic substances.

### *2.3.2 Environmental concentrations*

There are no data regarding inorganic chloramine concentrations in ambient air, groundwater, sediments, soils or biota. TRC, TRO, monochloramine and dichloramine have been measured in effluents containing municipal wastewater and drinking water, in cooling water, and in potable water, as well as in surface water near WWTP outfalls (see Pasternak and Powell, 2000). The following summarizes TRC and CRC concentrations in municipal wastewater and drinking water and in surface waters near WWTP outfalls.

#### 2.3.2.1 Effluent releases

Environment Canada (1997e) measured TRC, FRC, monochloramine, dichloramine and total organic chloramine concentrations at three sewage treatment plants in British Columbia in 1997. These three plants perform dechlorination prior to discharging treated wastewater. During this study, wastewater samples collected after chlorination and prior to dechlorination were analyzed for CRC species. Table 4 indicates that TRC was composed predominantly of inorganic and/or organic chloramines. This is substantiated by other studies presented in this section.

Based on a screening of approximately 50 riverine sites across Canada receiving chlorinated municipal WWTP effluent using average 1996 effluent data and mean annual river flow rates, it was found that effluents were diluted by a median value of approximately 940 times. During low flow, the median dilution was approximately 310 (range 2–50 000) (Pasternak and Powell, 2000). As a result, chloramine concentrations in effluents may be quickly diluted to non-detectable levels (approximately <0.01 mg/L) if rapid mixing occurs in a sufficient volume of surface water. However, at low dilutions and under conditions of slow chloramine decay (e.g., water with low organic material, low temperature and low total suspended solids), elevated chloramine concentrations may persist for great distances downstream from their source.

During the summer of 1998, Environment Canada contracted sampling studies at three riverine sites with low dilution (Sheep River, Don River and Lynne River) and at one lake site (Lake Ontario) with high loading and high dilution. In the Sheep River, at the Okotoks WWTP, Okotoks, Alberta, the CRC concentration at the sewage treatment plant's outfall was measured at 0.330 mg/L. At 5 m from the outfall, the CRC concentration ranged between <0.005 mg/L (the detection limit) and 1.350 mg/L. At 150 m downstream, CRC concentrations ranged from below the detection limit to 0.150 mg/L (Golder Associates Ltd., 1998).

At the Ashbridges Bay WWTP, the CRC concentration in the effluent was 1.250 mg/L, which dropped to 0.090–0.180 mg/L at 100 m from the outfall in Ashbridges Bay, Lake Ontario. The CRC concentration 1300 m away from the outfall ranged from 0.020 to 0.030 mg/L. At the North Toronto WWTP, the CRC concentration in the effluent was measured at 1.040 mg/L. The CRC concentration in the Don River 30 m downstream from the outfall was found to be <0.005–0.053 mg/L. At 200 m downstream, the CRC concentration was measured at <0.005–0.013 mg/L. The Simcoe WWTP effluent's CRC concentration ranged from 0.170 to 0.343 mg/L. In the Lynn River 3 m downstream from the plant's outfall, the CRC concentration ranged from <0.005 to 0.260 mg/L. At approximately 500 m downstream from the outfall, the CRC concentration in the Lynn River was <0.005 mg/L. Detectable chloramine concentrations were then measured at approximately 300 m downstream from the outfall. A subsequent, confirmatory sample at

**TABLE 4** Chloramine speciation at three municipal WWTPs in British Columbia[1]

| Item | Concentration (mg/L) | | |
|---|---|---|---|
| | Ladysmith Sewage Treatment Plant | Joint Abbotsford-Matsqui Environmental System | Kamloops Sewage Treatment Plant |
| | Primary treatment | Secondary treatment | Tertiary treatment (P removal) |
| Free residual chlorine | <0.02 | <0.02 | <0.02 |
| Monochloramine[2] | 0.407 | 0.026 | 0.414 |
| Dichloramine[2] | 0.02 | <0.02 | 0.374 |
| Total organochloramine[3] | 0.783 | 0.058 | 0.017 |
| Total residual chlorine | 1.21 | 0.084 | 0.805 |

[1] Sampling of effluent was conducted in the effluent pipe after chlorination, but before dechlorination. None of these facilities released measurable chlorine residual concentrations to the environment. Each facility dechlorinates at all times when they chlorinate.

[2] Analysis for monochloramine and dichloramine by HPLC with post-column amperometric detection. Analysis for FRC and TRC by DPD-FAS titration method.

[3] Estimated total organic chloramine = TRC – FRC – monochloramine – dichloramine (Environment Canada, 1997e).

600 m downstream, however, contained CRC concentrations of 0.020–0.023 mg/L. Sampling at the 300-m site disturbed the bottom sediments and may have caused the resuspension of chloramines into the water column. This resuspended chloramine may have been measured at the 600-m site. These observations suggest that chloramines may be stored in the sediments of a river and could be released if the sediments are disturbed (Gartner Lee Ltd., 1998).

Wisz *et al.* (1978) studied the decay of residual chlorine in the receiving waters at four Ontario municipal WWTPs (at Aurora, Bolton, Brantford and Alliston). The downstream persistence of residual chlorine was noted to depend largely on dilution. Relatively fast degradation of residual chlorine occurred in receiving waters where the dilution ratio was greater than 20:1. During the summer study period, under low-flow stream conditions, the dilution ratios at the selected facilities were as follows: Brantford 43:1, Alliston 23:1, Aurora 1:1.3 and Bolton 24.6:1. Two receiving streams showing rapid degradation were the Grand River (Brantford WWTP) and the Boyne River (Alliston WWTP). TRC concentrations at the two outfalls of the Brantford WWTP were 0.880–2.288 mg/L and 0.920–2.272 mg/L, respectively. At 107 m downstream, the TRC concentration in the Grand River was already approaching the detection limit of 0.002 mg/L. At 942 m, there were no measurable concentrations of TRC. At the Alliston WWTP outfall, the TRC concentrations ranged from 0.768 to 1.408 mg/L. Downstream at 61 m, the TRC concentration had declined to <0.002–0.045 mg/L; at approximately 1.5 km, the TRC concentration was below the detection limit.

Wisz *et al.* (1978) showed that chloramine decay is substantially slower in the winter than during the summer. In the summer of 1976, the monochloramine and dichloramine concentrations at the Aurora WWTP outfall ranged from 1.120 to 1.440 mg/L and from below the detection limit to 0.144 mg/L, respectively. At 91 m downstream in Aurora Creek, monochloramine concentrations ranged from 0.364 to 0.632 mg/L. At 2900 m downstream, monochloramine concentrations fell below detection limits (<0.002 mg/L). Dichloramine was measured at approximately 2900 m downstream from the outfall (0.013–0.018 mg/L). In the winter of 1977,

monochloramine and dichloramine concentrations measured at the Aurora Creek outfall were 1.200 and 0.320 mg/L, respectively. At 4800 m downstream from the outfall, the concentrations of monochloramine and dichloramine were 0.216 and 0.080 mg/L, respectively.

2.3.2.2 Drinking water releases

Sampling studies were conducted by Environment Canada and the Fraser Valley Regional District (FVRD) in Mission and Abbotsford, British Columbia, to determine whether chloramines from outdoor residential water use and from industrial washdown activities could be measured in local waterways (Vanden Berg and Wade, 1997; FVRD, 1998, 1999; Pasternak *et al.*, 1998, 1999). Measurable concentrations of CRC and FRC were not found at outlets of storm drains and in local streams using HPLC, DPD FAS and amperometric titration methods. These studies did not substantiate the findings of Triton Environmental Consultants Ltd. (1995), who found measurable TRC and FRC concentrations at several of the same streams using the Hach Kit DPD colorimetric method. The reports, with the exception of Triton Environmental Consultants Ltd. (1995), concluded that low-discharge uses of chloramine-treated water (e.g., lawn and garden watering, car washing, driveway washing and equipment washing) do not result in measurable levels of chloramines in surface waters of the FVRD.

Two major salmonid and invertebrate kill events resulting from the release of chloramine-treated drinking water via main breaks to Fergus Creek (Surrey, British Columbia) indicate that levels of inorganic chloramines that are acutely lethal to salmonids and invertebrates have occurred in surface waters (see Section 2.4.1.3). TRC concentrations in the chloraminated drinking water from the area of each main break were 2.53 and 2.75 mg/L (Nikl and Nikl, 1992). These events resulted in *Fisheries Act* convictions.

## 2.4 Effects characterization

### *2.4.1 Ecotoxicology*

A thorough review of the international literature regarding the environmental toxicology of inorganic chloramines has been completed in which relevant toxicological information was summarized, important data gaps were identified and numerical data quality rankings were assigned to relevant articles (see Farrell and Wan, 2000: Appendix B).

2.4.1.1 Mode of action

Monochloramine affects protein-associated processes in bacteria, and the mode of action appears to be a "multiple-hit mechanism" involving the inactivation of several sites before cell death or irreversible injury occurs (Jacangelo *et al.*, 1991). Amino acids, especially those with sulfur groups and tryptophan, were found to be more reactive than the nucleic acids in disinfection studies (Ingols *et al.*, 1953; Boyce, 1963). Monochloramine inhibited bacterial growth as well as DNA, RNA and protein synthesis at levels of 0.515 mg/L. At a monochloramine concentration of 5.15 mg/L, enzymes that contained sulfhydryl groups were significantly inhibited (Kohl *et al.*, 1980). Monochloramine inhibition was found to be irreversible with the addition of sulfhydryl-containing chemicals after the addition of monochloramine. It was speculated that monochloramine probably acts on other sites in addition to the sulfhydryl groups (Boyce, 1963; Kohl *et al.*, 1980).

Studies on the mode of action of monochloramine in viruses are limited. Two mechanisms have been shown. One involves the interaction of monochloramine with the RNA in a bacteriophage, and the other involves the interaction of a mixture of inorganic chloramines with the protein coat of the virus. The mode of action in viruses may vary with virus type and chloramine concentration (Fujioka *et al.*, 1980; Olivieri *et al.*, 1980).

Chloramines appear to cross the fish gill epithelium quite readily and do not cause significant cellular damage in comparison with free chlorine. In fish, inorganic chloramines affect transport of oxygen in blood by reacting with the hemoglobin of the red blood cells to form methemoglobin, inhibiting the cell's ability to bind oxygen (Buckley, 1976). The percentage of methemoglobin within the hemoglobin increases significantly with exposure to chloramines, and the fish begins to exhibit signs of hemolytic anemia. Severe hemorrhaging occurs throughout the body and from the fins. In addition, the body of the fish becomes covered with a mucous coating, and the fish shows increased "coughing" and erratic swimming (Grothe and Eaton, 1975; Buckley, 1977; Travis and Heath, 1981). Inorganic chloramines have also been found to reduce filtration and reproduction in rotifers, lobsters and fish, but the underlying mechanisms for the responses are not clear (Capuzzo *et al.*, 1976, 1977; Capuzzo, 1977, 1979a).

Certain fish are able to avoid chloramines at levels ranging from 0.0057 to 0.44 mg/L (Fava and Tsai, 1978; Cherry *et al.*, 1979; Hidaka and Tatsukawa, 1985). However, some fish species have demonstrated a reduced avoidance response at a preferred temperature. Warmer temperatures may counteract the avoidance response and result in fish attraction (Hall *et al.*, 1982, 1983). The excess ammonia that is used to create inorganic chloramine solutions may also attract some fish species, thereby mitigating the avoidance response to inorganic chloramine (Cherry *et al.*, 1982). Finally, some fish are capable of detecting lower inorganic chloramine levels if allowed longer exposure periods, during which time they acquire avoidance response skills (Fava and Tsai, 1978).

#### 2.4.1.2 Terrestrial organisms

Studies of inorganic chloramine toxicity (acute or chronic) to plants are limited. A study on horse bean (*Vicia faba*) seeds showed that a 60-minute exposure to monochloramine at a concentration of 5.15 mg/L resulted in 24% abnormal anaphases. It appears that monochloramine can induce chromosome damage at concentrations that do not cause visible damage to the plant (Sekerka, 1981).

There are very few inorganic chloramine toxicity data (acute or chronic) available for terrestrial animals, with the exception of rats (Farrell and Wan, 2000: Appendix A). Only one study was found examining the effects of inorganic chloramines on amphibians. This study, which utilized eggs from the urodele amphibian, *Pleurodeles waltl*, found that monochloramine caused mutations at a concentration of 0.15 mg/L but not at 0.05 or 0.01 mg/L (Fernandez *et al.*, 1993).

#### 2.4.1.3 Aquatic organisms

The acute toxicity of inorganic chloramines to aquatic organisms is species-specific and is a function of life stage, chemical species, exposure duration, pH and temperature. Variability in test conditions (e.g., differences in pH, temperature, exposure duration and inorganic species composition) and data quality makes comparisons between historical inorganic chloramine toxicity values quite difficult. Particular concern exists over the variable and imprecise ways in which inorganic chloramine concentrations were reported. Also, synergism between free chlorine toxicity and inorganic chloramine toxicity may occur (Farrell and Wan, 2000: Appendix A).

To summarize the available data, determine sensitive aquatic species and identify data gaps, a meta-analysis approach (Mattice and Zittel, 1976; Mattice, 1977) was used in which all aquatic toxicity data were graphically represented by plotting $LC_{50}$ values as a function of exposure time according to biological and environmental categories (see Farrell and Wan, 2000: Appendix C). These graphs were intended to establish a lower-boundary concentration line above which lay all acute toxicity data, including those for sensitive species. However, this objective was not realized, because no single species had a sufficiently comprehensive data set to allow a lower boundary line for inorganic chloramine concentration to be set with confidence.

Consequently, supplementary acute toxicity testing, supported by the best available analytical chemistry, was performed with representative freshwater fish (juvenile chinook salmon, *Oncorhynchus tshawytscha*) and invertebrates (*Ceriodaphnia dubia* and *Daphnia magna*) and marine invertebrates (*Amphiporeia virginiana* and *Eohaustorius washingtonianus*). Time-to-lethality (e.g., $LT_{100}$, $LT_{50}$, $LT_{20}$, $LT_0$) reference lines were determined for these species.

#### *2.4.1.3.1 Freshwater and marine algae and plankton*

Inorganic chloramines are used for the control of freshwater and marine fouling, bacterial growth and planktonic growth. According to Farrell and Wan (2000: Appendix A), the lowest reported observed effect concentration produced by residual chlorine on a species of algae is 0.01 mg/L. This corresponded to a 15-minute $EC_{50}$ (carbon uptake) for the unicellular alga *Pyramimonas virginica* (Bender *et al.*, 1977). Maruyama *et al.* (1988) found 10-day $EC_{50}$s (growth) of 0.014 and 0.02 mg/L for the multicellular red alga *Porphyra yezoensis*.

#### *2.4.1.3.2 Freshwater invertebrates*

The $LC_{50}$ values for invertebrates ranged from 0.011 mg/L for the freshwater water flea, *D. magna* (24-hour $LC_{50}$), to 0.96 mg/L for the freshwater crayfish, *Oronectes nais* (96-hour $LC_{50}$) (Ludwig, 1979; Kaniewska-Prus, 1982). The reported $LC_{50}$ values for *D. magna* varied considerably (e.g., 24-hour $LC_{50}$ values ranged from 0.011 to 0.110 mg/L). Therefore, supplementary acute toxicity tests were performed with *D. magna* in conjunction with the best available analytical chemistry to ascertain the reliability of literature values; the results of these tests are summarized in Farrell and Wan (2000). The estimated 24-hour and 48-hour $LC_{50}$ values for *D. magna* were 0.019 mg/L and 0.017 mg/L for inorganic chloramines, respectively, in 20°C water at pH 8. These $LC_{50}$ values were comparable to the lowest of the existing $LC_{50}$ values for *D. magna* published in the literature. However, the rotifer, *Keratella cochlearis* (24-hour $LC_{50}$ 0.0135 mg/L), and the Australian water flea, *C. dubia* (24-hour $LC_{50}$ 0.012 mg/L), were more sensitive than *D. magna* to continuous chloramine exposures (Beeton *et al.*, 1976; Taylor, 1993). In contrast, the Asiatic clam, *Corbicula fluminea*, was very resistant, with an $LC_{50}$ value greater than 2 mg/L (Belanger *et al.*, 1991).

Using data from the open literature, too few data points existed for a single sensitive species to permit a lower-boundary concentration line for continuous chloramine toxicity to freshwater invertebrates to be defined with confidence. Therefore, comprehensive time-to-50%-lethality ($LT_{50}$) tests with *C. dubia*, the second most sensitive freshwater invertebrate, were conducted. These supplementary tests were supported by the best available analytical chemistry; although static exposures were used, water replacement every hour limited chloramine degradation over time in the test chambers (Farrell and Wan, 2000: Appendix E). For exposures up to 3200 minutes for 26 monochloramine concentrations, the $LC_{50}$ for third-generation neonate (12–24 hours old) *C. dubia* was predicted by a simple exponential equation:

$$LC_{50}\ (mg/L) = 61.6t^{-1.08} \quad (1)$$

where t = exposure time in minutes ($R^2 = 0.95$).

For times to lethality for 20% of *C. dubia*, the following exponential equation was derived by Farrell and Wan (2000: Appendix C):

$$LC_{20}\ (mg/L) = 53.9t^{-1.10} \quad (2)$$

where t = exposure time in minutes ($R^2 = 0.92$).

The $LT_{50}$ and the $LT_{20}$ curves for *C. dubia* are depicted in Figures 5 and 6.

#### *2.4.1.3.3 Marine invertebrates*

The available acute toxicity data for marine/estuarine invertebrates are highly variable.

**FIGURE 5** $LT_{50}$ curve fitted to data for the effects of inorganic chloramines on *Ceriodaphnia dubia* (Farrell and Wan, 2000: Appendix C)

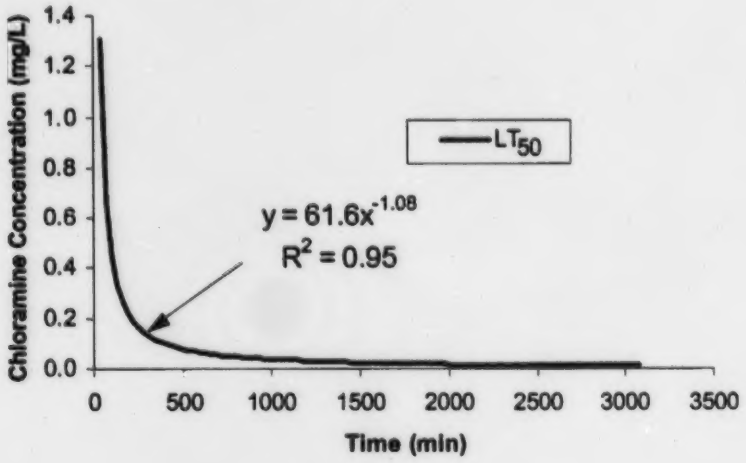
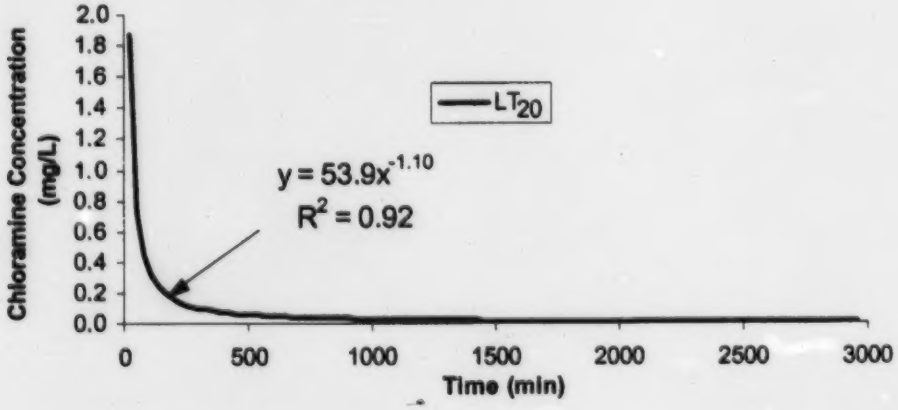



**FIGURE 6** $LT_{20}$ curve fitted to data for the effects of inorganic chloramines on *Ceriodaphnia dubia* (Farrell and Wan, 2000: Appendix C)




Nevertheless, this grouping contained data for species that seemed to be extremely sensitive to inorganic chloramines (i.e., 48-hour $LC_{50}$ of <0.01 mg/L for juveniles and larvae of an oyster, *Crassostrea virginica*, and 48-hour $LC_{50}$ of 0.001 mg/L for larvae of a clam, *Mercenaria mercenaria*) (Bender *et al.*, 1977; Capuzzo, 1979b). The acute toxicity of CPO to two marine invertebrates, *A. virginiana* and *E. washingtonianus*, was studied (Farrell and Wan, 2000: Appendix E) using the best available resources (test species and analytical chemistry). The estimated 48-hour $LC_{50}$ values for *A. virginiana* and *E. washingtonianus* were 0.567 mg/L and 0.626 mg/L, respectively, while the 168-hour $LC_{50}$ values were 0.043 mg/L and 0.134 mg/L, respectively, in 10°C and 15°C seawater at pH 7.5.

#### 2.4.1.3.4 *Freshwater fishes*

In terms of acute toxicity at comparable exposure durations, the most sensitive freshwater invertebrate species was almost 10 times more sensitive to inorganic chloramines than the most sensitive fish species. Ninety-six-hour $LC_{50}$ values for fish ranged from 0.07 mg/L for coho salmon (*Oncorhynchus kisutch*) to 1.72 mg/L for carp (*Cyprinus carpio*) (Buckley, 1976; Heath, 1977).

Fish species have shown an inverse relationship between temperature and monochloramine resistance (Roseboom and Rishey, 1977; Seegert *et al.*, 1979; Elmore *et al.*, 1980). The temperature at which this relationship starts to take effect is very dependent on species and the temperature range within which the species functions most effectively. Some organisms may show eurythermal adaptation, which is the ability to shift lethal limits, reproduction and metabolic activities to allow tolerance of a wide range of thermal stresses. Several instances of greater chloramine tolerance by cold-water fish species, such as brook trout (*Salvelinus fontinalis*), in comparison with warm-water fish species, such as channel catfish (*Ictalurus punctatus*), have been observed (Heath, 1977). This is in direct conflict with the general supposition that cold-water salmonids are the most sensitive to chlorine compounds (Farrell and Wan, 2000: Appendix A).

The evaluation of the effects of pH, by regression analyses of chlorine bioassay data, on CRC toxicity in fresh water (pH 5–8) indicates that changes in pH modify the extent of effluent toxicity only slightly (Farrell and Wan, 2000: Appendix A).

Dichloramine solutions appear to be more toxic to fish than monochloramine solutions, although a few exceptions have been found. Trichloramine species are very rarely found in the environment (Thomas *et al.*, 1980; Brooks and Bartos, 1984).

The effects of inorganic chloramines on various life stages (alevin, fry, juvenile) of brook trout and coho salmon have been examined. The alevin life stage was more tolerant of inorganic chloramines than the fry, with larger, older alevins being less tolerant than the newly hatched alevins. The greatest sensitivity to inorganic chloramines was observed just after the fry stage. This may be due in part to the physiological and behavioural stresses related to the change in feeding patterns (i.e., from using a yolk sac to foraging for food) that occurs at that point in the fish life cycle.

Post-exposure mortality was limited to toxicity tests of less than 200 minutes in duration. Intermittent chloramine exposure was either less toxic than or as toxic as continuous exposure.

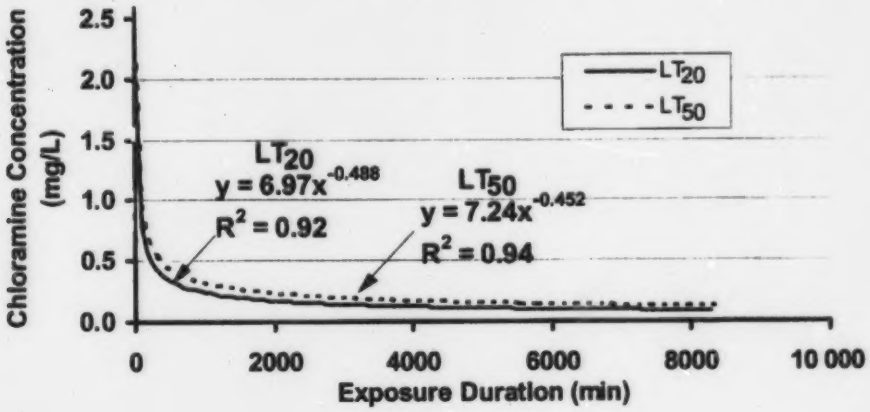
The lowest No-Observed-Adverse-Effect Concentration (NOAEC) for inorganic chloramines for fish was 0.0165 mg/L for the fathead minnow (*Pimephales promelas*). The threshold for growth reduction in coho salmon was 0.011–0.023 mg inorganic chloramines/L. By comparison, avoidance behaviour data existed for 12 species. Thresholds for adult coho salmon and rainbow trout (*Oncorhynchus mykiss*) appeared to be at 0.090–0.110 mg/L for a 10-minute exposure, but alewife (*Alosa pseudoharengus*) detected chloramines at 0.002 mg/L in a 45-minute exposure.

To define a lower-boundary concentration line for continuous chloramine toxicity, $LT_{50}$ tests with juvenile chinook salmon were conducted (Farrell and Wan, 2000). There were insufficient data from the literature to allow a lower-boundary concentration line for continuous chloramine toxicity to be defined with confidence without these further tests. For exposures up to 10 days, the $LC_{50}$ was predicted by a simple exponential equation:

$$LC_{50}\ (mg/L) = 7.24t^{-0.452} \qquad (3)$$

where t = exposure time in minutes ($R^2 = 0.94$).

**FIGURE 7** $LT_{20}$ and $LT_{50}$ curves fitted to data for the effects of inorganic chloramines on juvenile chinook salmon (*Oncorhynchus tshawytscha*) (Farrell and Wan, 2000: Appendix B)




The projected incipient lethal concentration for 50% mortality of juvenile chinook salmon was 0.09 mg/L for exposure durations of no longer than 10 days. Chloramine exposures of <0.67 mg/L for up to 3 hours produced no post-exposure mortality.

For chinook salmon exposed up to 10 days, the $LC_{20}$ was fitted to the observed toxicity data by the exponential equation:

$$LC_{20}\ (mg/L) = 6.97t^{-0.488} \qquad (4)$$

where t = exposure time in minutes ($R^2 = 0.92$).

The $LT_{50}$ and $LT_{20}$ curves for chinook salmon are presented in Figure 7. When equations 1 and 2 for *C. dubia* are compared with equations 3 and 4 for chinook salmon, it is clear that juvenile chinook salmon are less sensitive to inorganic chloramines than *C. dubia*.

### *2.4.1.3.5 Marine/estuarine fishes*

Toxicity data regarding marine and estuarine fishes are few. The silverside (*Menidia menidia*) was the most sensitive marine/estuarine species (96-hour $LC_{50}$ 0.040 mg/L) (Bender *et al.*, 1977). The effects of inorganic chloramines (measured as total chlorine) on three species of juvenile marine fish — winter flounder (*Pseudopleuronectes americanus*), scup (*Stenotomus versicolor*) and killifish (*Fundulus heteroclitus*) — were investigated by Capuzzo *et al.* (1977) at 25°C and 30°C. Inorganic chloramines were found to be the most toxic to killifish (100% mortality at 1.20 mg residual chloramine/L), followed by winter flounder (100% mortality at 2.55 mg/L) and scup (100% mortality at 3.10 mg/L). Stress was observed at 0.65 mg residual chloramine/L for killifish, 1.50 mg/L for winter flounder and 2.20 mg/L for scup. A synergistic effect between inorganic chloramine toxicity and temperature was observed, as increasing the temperature to 30°C caused 100% mortality to be observed at lower inorganic chloramine concentrations.

### *2.4.2 Abiotic atmospheric effects*

Inorganic chloramines are formed in and released to aquatic environments. Although they are known to volatilize, there are no literature-reported chloramine concentrations in ambient air. Inorganic chloramines absorb radiation in the 200–300 nm wavelength region of the spectrum, and they are susceptible to photolysis in water (Hand and Margerum, 1983; Lin *et al.*, 1983; Reckhow *et al.*, 1990). There are no data pertaining to inorganic chloramine fate in the atmosphere, although there are reports that they

are very unstable and not persistent in the atmosphere (Kirk-Othmer, 1979; Lide, 1998). Monochloramine and dichloramine are very water soluble and hence susceptible to removal from the atmosphere by scavenging rain and subsequent deposition to soil and water. The combined effect of atmospheric reactivity and rain scavenging would inhibit the involvement of monochloramine and dichloramine in stratospheric ozone layer depletion. Also, the available information indicates that chloramines would make a negligible contribution to tropospheric ozone formation.

# 3.0 Assessment of "Toxic" under CEPA 1999

## 3.1 CEPA 1999 64(a): Environment

The environmental risk assessment of PSL substances is based on the procedures outlined in Environment Canada (1997a). Analysis of exposure pathways and subsequent identification of sensitive receptors are used to select environmental assessment endpoints (e.g., adverse reproductive effects on sensitive fish species in a community). For each endpoint, a conservative Estimated Exposure Value (EEV) or Estimated Environmental Concentration (EEC) is selected and an Estimated No-Effects Value (ENEV) is determined by dividing a Critical Toxicity Value (CTV) by an application factor. A conservative (or hyperconservative) quotient (EEV/ENEV or EEC/ENEV) is calculated for each of the assessment endpoints in order to determine whether there is potential ecological risk in Canada. If these quotients are less than one, it can be concluded that the substance poses no significant risk to the environment, and the risk assessment is completed. If, however, the quotient is greater than one for a particular assessment endpoint, then the risk assessment for that endpoint proceeds to an analysis where more realistic assumptions are used and the probability and magnitude of effects are considered. This latter approach involves a more thorough consideration of the sources of variability and uncertainty in the risk analysis.

### *3.1.1 Assessment endpoints*

In Canada, releases of inorganic chloramines are in aqueous solution destined for aquatic environments. Hence, this assessment is based on water-phase exposures. Trichloramine is not of environmental significance, since conditions rarely occur that support its formation. Because inorganic chloramines are in dynamic equilibrium with other residual chlorine species, and due to analytical limitations that usually preclude species-specific analysis, this assessment often uses data pertaining to TRC and TRO. In reality, observed effects are usually as a result of the simultaneous presence of different chlorine residuals whose individual effects are indistinguishable.

Releases of inorganic chloramines to surface waters are due to effluent, cooling water and potable water releases. However, some drinking water releases (e.g., due to outdoor water use, main breaks and leaks) are to soils.

Both monochloramine and dichloramine are water soluble and are known to volatilize into the air phase and partition to or react with sediments. However, there are no data regarding their presence or fate in air and sediment phases. Impacts due to residual chlorine have not been documented in any phase except for the water phase. Historically, their presence in air and sediment phases has not appeared to be as great a concern as concentrations in surface waters. Therefore, this assessment will focus on the water-phase exposures of inorganic chloramines.

Decay data indicate that inorganic chloramines are not persistent in the environment; thus, the assessment of releases focuses on exposures near point sources and acute and subacute effects on receptor organisms.

#### 3.1.1.1 Releases to soils

The assessment endpoint for soils was mortality/recovery of microorganisms and soil processes. Soil microorganisms are important for nutrient cycling and decomposition of organic matter and are thus important for plant growth. Reductions in microbial populations can inhibit plant growth.

#### 3.1.1.2 Releases to water

Assessment endpoints for surface waters (fresh water and seawater) include the survival of sensitive invertebrates and fish. Invertebrates are an essential component of aquatic ecosystems. Benthic invertebrates (e.g., amphipods and isopods) facilitate detrital decomposition. Both benthic and pelagic invertebrates consume bacteria and phytoplankton and themselves serve as sources of food for many fish species. For instance, cladocerans from the family Daphniidae, which includes *Daphnia* spp. and *Ceriodaphnia* spp., are ubiquitous in temperate lakes and ponds, as well as in quiescent sections of streams and rivers throughout North America. Daphnids are often more sensitive than other aquatic organisms to various chemicals and as such are good surrogates for the protection of other aquatic life. Cladocerans are ecologically important species, since they convert phytoplankton and bacteria into animal protein (Environment Canada, 1992). They are representative of other larger and smaller invertebrates that together act as food sources for many fish. They also form a significant portion of the diet of many fishes, including salmonids, which are themselves an important food, economic and cultural resource for Canadians. Some birds and terrestrial mammals also depend on the presence of fish as a food source.

Saltwater invertebrates are equally important to the functioning of marine and estuarine ecosystems. Amphipods are an abundant component of benthic communities in estuarine and marine environments and are a primary food source for certain species of whales and for many species of birds, fish and larger invertebrates. *Amphiporeia virginiana* and *E. washingtonianus* are two important and commonly found amphipods in Canadian waters. Marine fish serve as an important food, economic and cultural resource for Canadians.

### *3.1.2 Environmental risk characterization*

It was determined that the assessment in soils would be qualitative at the hyperconservative level rather than follow the quotient approach, since the available data did not facilitate a quantifiable approach.

The risk assessment in surface water followed a tiered risk assessment approach as identified in the guidance manual (Environment Canada, 1997a).

#### 3.1.2.1 Soil organisms

No information is available that was directly relevant to the effects of inorganic chloramines in soils. However, the available evidence indicates that negative impacts on soil microorganisms from inorganic chloramines are unlikely. First, a proportion of the inorganic chloramine would be lost prior to entering the soil environment (e.g., from volatilization, photolysis, reaction with particulates) and hence would not come into contact with soil microbes. Upon infiltrating soils, the treated water would be exposed to a variety of organic materials that are extremely reactive with inorganic chloramines. These organic substances serve as effective reducing agents that change the form of inorganic chloramines and bind them to the soil matrix. Although there are limited data regarding these transformation products and their toxicity, their disinfection potential is usually considered limited. According to Zellmer *et al.* (1987), hypochlorous acid applied in the form of calcium hypochlorite will be immobilized and deactivated by a mineral soil (i.e., fine-silty clay loam).

The disinfection molecule in aqueous solution must come into contact with the microorganism in order for inactivation to occur. The presence of particulates can provide protection to microorganisms against disinfectants. The protection afforded bacteria associated with surface solids would most likely result from physical interference with the transport of the chloramine molecules towards the organism, because of a barrier of charges associated with the particulate (Gerba and Stagg, 1979). Microorganisms embedded in particulate matter may be afforded significant protection from a disinfectant (Berman *et al.*, 1988).

In addition, it should be noted that there have been no historic accounts of environmental impacts resulting from inorganic chloramine release to soils or to any phase other than water.

Since populations of soil microorganisms and soil processes are not likely to be harmed from the application of inorganic chloramines to soils, the assessment of chloramine risk in soils did not proceed to Tier 2.

3.1.2.2 Aquatic organisms

*3.1.2.2.1 Hyperconservative risk assessment*

Receptors and assessment endpoints

For the hyperconservative assessment, the CTV was based on the most sensitive species receptor, and the assessment endpoint was mortality. The value of 0.01 mg/L was the lowest concentration resulting in the mortality of 50% of a test population found in the published literature respecting freshwater and marine biota based on the initial review of the literature. Kaniewska-Prus (1982) exposed *D. magna* to chloramines (80% monochloramine, 17% dichloramine and 3% trichloramine, measured by the orthotolidine method; see Kaniewska-Prus and Sztrantoicz, 1979) in a static freshwater bioassay and derived a 24-hour $LC_{50}$ of 0.0108 mg/L. Capuzzo (1979b) exposed the American oyster, *C. virginica*, to chloramines in continuous-flow seawater bioassays and derived a 30-minute $LC_{50}$ of 0.01 mg/L. The concentration 0.01 mg/L was then divided by an application factor to translate it to an ENEV. There are no rules for the selection of an application factor, but Environment Canada (1997a) suggests a maximum application factor of 100 for converting the lowest acute $LC_{50}$ or $EC_{50}$ from a data set to a hyperconservative ENEV. Therefore, the hyperconservative ENEV = 0.0001 mg/L (0.01 ÷ 100).

Hyperconservative assessment of chloramine exposure from effluents, cooling waters and drinking water

The hyperconservative evaluation was conducted early in the assessment process when there were very few data regarding inorganic chloramine concentrations in aquatic environments. As a result, maximum end-of-pipe concentrations were used as freshwater and saltwater EEVs. Based on the data available at the time, the hyperconservative EEVs were 3.0 mg/L for drinking water, 3.56 mg/L for chlorinated municipal effluent and 2.0 mg/L for chlorinated cooling water from electrical utilities. These represented maximum TRC concentrations described by various sources (Norecol Environmental Consultants Ltd. and Dayton and Knight Ltd., 1992; Government of Canada, 1993). TRC was used as a surrogate for inorganic chloramine since, in a worst-case scenario, all TRC present could be in the form of inorganic chloramine.

Using the above-indicated EEVs and ENEV, the following hyperconservative quotients were derived:

- treated potable water at its source:
  3.0 mg/L ÷ 0.0001 mg/L = 30 000
- chlorinated municipal effluent:
  3.56 mg/L ÷ 0.0001 mg/L = 35 600
- chlorinated cooling water:
  2.0 mg/L ÷ 0.0001 mg/L = 20 000

Quotients exceeded 1 by very large margins. Hence, the risk assessment for inorganic chloramine in surface waters proceeded to a conservative-level assessment.

*3.1.2.2.2 Conservative risk assessment*

Receptors and assessment endpoints

A conservative approach was taken for the derivation of ENEVs using the most sensitive freshwater and saltwater species. This involved

**TABLE 5** Calculation of no-effects factors used in conservative assessments

| Time (hours) | Time (minutes) | $LC_{50}$ (mg/L) | $LC_0$ (mg/L) | No-effects factor[1] |
|---|---|---|---|---|
| 8 | 480 | 0.0809 | 0.0412 | 0.51 |
| 48 | 2880 | 0.0118 | 0.0074 | 0.63 |

[1] No-effects factor = 8-hour $LC_0$/8-hour $LC_{50}$ and 48-hour $LC_0$/48-hour $LC_{50}$.

a rigorous evaluation of existing data and newly available data provided through additional acute toxicity testing, supported by the best available analytical chemistry (see Farrell and Wan, 2000: Appendices B–F).

The ENEVs derived for the conservative assessment were based on the recommendations identified in Appendix H in Farrell and Wan (2000). The ENEVs were derived for *C. dubia* because it was more sensitive to monochloramine than chinook salmon for exposure times greater than 1 hour and because, as a group, invertebrates were found to be many times more sensitive to inorganic chloramine and residual oxidant exposures than fish (Farrell and Wan, 2000). Although some freshwater and marine invertebrates from the open literature appeared to be more sensitive to monochloramine than *C. dubia*, the data set for *C. dubia* was very comprehensive. Using these data, Farrell and Wan (2000: Appendix H) derived a reference line (the lowest reference concentration for 50% lethality) against which to compare the sensitivity of other organisms. Using their analysis, an 8-hour $LC_{50}$ of 0.060 mg/L and an incipient $LC_{50}$ of 0.018 mg/L were derived for *C. dubia*. The incipient toxicity level is defined as the concentration of chemical that was lethal to 50% of the test organisms as a result of exposure for periods sufficiently long that the acute lethal action essentially ceases. The incipient level is also the asymptote of the toxicity curve or that part of the curve that is parallel to the time axis. The asymptote produced by the *C. dubia* $LC_{50}$ model occurred at 17.9 hours. Therefore, at times ≥17.9 hours, the $LC_{50}$ concentration (0.018 mg/L) remains essentially the same.

In order to account for data points that were below those of the *C. dubia* model, a species sensitivity application factor was used in conjunction with the incipient $LC_{50}$ (≥1073[1] minutes) of 0.018 mg/L. In keeping with the conservative approach of the Tier 2 assessment, it was still necessary to convert the $LC_{50}$ data to ENEVs. Farrell and Wan (2000: Appendix B) undertook monochloramine toxicity studies with *C. dubia* and derived power equations to describe the $LT_{50}$ and $LT_0$ data (valid for exposures of 10–3200 minutes).

Using these equations, the $LC_{50}$ and $LC_0$ are calculated for 8 hours and 48 hours, and the differences or ratios between the two values (i.e., 8-hour $LC_0$/8-hour $LC_{50}$ and 48-hour $LC_0$/48-hour $LC_{50}$) were used as application factors to calculate the ENEVs (see Table 5).

Therefore, the 8-hour ENEV for freshwater organisms can be calculated as follows:

ENEV = 0.060 mg/L × species sensitivity factor × no-effects factor

= 0.060 mg/L × 0.5 × 0.51

= 0.015 mg/L

The incipient ENEV (for durations ≥1073 minutes) for freshwater organisms can be calculated as:

[1] Rounding may result in values that are slightly different from those reported.

ENEV = 0.018 mg/L × species sensitivity factor × no-effects factor

= 0.018 mg/L × 0.5 × 0.63

= 0.0056 mg/L

The *C. dubia* mathematical model for acute toxicity was adopted as a point of reference for determining a suitable lower boundary line for marine invertebrates due to insufficient acute toxicity data with which to perform reliable modelling with marine and estuarine invertebrate species (Farrell and Wan, 2000). For the *C. dubia* mathematical model, a species sensitivity factor of 0.1 was recommended by Farrell and Wan (2000: Appendix G) for exposure times less than that of the "time to incipient $LC_{50}$" (i.e., 1073 minutes), and a species sensitivity factor of 0.25 was recommended for exposure times greater than 1073 minutes. These factors are suggested to account for CPO effects data identified in the open literature. In seawater, the addition of chloramines will result in the formation of bromamines. For marine environments, the species sensitivity factor of 0.25 was reasonable given that the $EC_{50}$ for sublethal effects on oyster larvae is <0.005 mg/L. Using the *C. dubia* mathematical model, an incipient $LC_{50}$ of 0.018 mg/L was predicted, and the species sensitivity factor of 0.25 lowers this to 0.0045 mg/L.

Using the *C. dubia* mathematical model for acute toxicity (Equation 1), the marine species sensitivity factors of 0.1 and 0.25 identified above and the no-effects factors identified in Table 5, ENEVs for saltwater organisms are calculated.

The 8-hour ENEV for saltwater organisms is calculated as follows:

ENEV = 0.060 mg/L × marine species sensitivity factor × no-effects factor

= 0.060 mg/L × 0.1 × 0.51

= 0.0031 mg/L

The incipient ENEV (for durations ≥1073 minutes) for saltwater organisms is calculated as:

ENEV = 0.018 mg/L × marine species sensitivity factor × no-effects factor

= 0.018 mg/L × 0.25 × 0.63

= 0.0028 mg/L

Conservative assessment of chloramine exposure from effluents and cooling water

The assessment of chloramines is national in scope, with a diversity of discharge and exposure scenarios. To facilitate and simplify the risk assessment, discharges with similar characteristics were grouped together into discharge categories. Assessments were conducted for discharges in each category (see Table 6).

There were insufficient measured concentrations to screen chloramine exposures in the environment. Hence, the conservative assessment focused largely on estimated data produced from mathematical models (see McCullum *et al.*, 2000; Pasternak, 2000). For effluents, the purpose was to screen characteristics of chloramine discharges into Canadian surface waters and identify which discharge settings may have the greatest impact on receiving aquatic environments. Mixing models appropriate for describing the dispersive behaviour of residual chloramines in surface waters were used on a number of specific settings.

Characteristics of chloramine discharges from over 110 WWTPs were screened to identify the highest chloramine discharge loadings to surface waters. The highest discharge loading of chloramines (measured as TRC) in each of four regions of Canada was retained for modelling. These regions included western/coastal, Prairie, Great Lakes, and eastern/coastal. Eighteen discharge settings (12 wastewater, 5 drinking water treatment and 1 cooling water) in Canada were subjected to residual chloramine dispersion

**TABLE 6** Matrix of different discharge situations

| Type | Characteristic | Fresh water | | | Salt water |
|---|---|---|---|---|---|
| | | Small stream [1] | Large stream [2] | Lake | Estuary/marine |
| Drinking water | • short, often unpredictable<br>• intermittent | • leaks/breaks<br>• outdoor uses<br>• plant wastes | • leaks/breaks<br>• outdoor uses<br>• plant wastes | • leaks/breaks<br>• outdoor uses<br>• plant wastes | • leaks/breaks<br>• outdoor uses<br>• plant wastes |
| Effluent | • continuous | NA | • sewage | • sewage | • sewage |
| Cooling water | • intermittent | | • cooling water | • cooling water | • cooling water |

[1] Small streams are subjectively defined to have an annual average water flow rate of ≤1.0 $m^3/s$.

[2] Large streams are subjectively defined to have an annual average water flow rate of >1.0 $m^3/s$.

modelling in surface waters under defined conditions (see McCullum *et al.*, 2000).

In keeping with the conservative intent, all effluent and cooling water discharges were treated equally as continuous discharges, even though some were intermittent. Also, inorganic chloramine decay was assumed to be slow (1 per day, half-life of 0.69 days). Hydrological data (flow rate, current velocity, depth and width) represented 20-year arithmetic means for the period 1976–1995, or shorter periods if there were insufficient data to determine the 20-year average. TRC was modelled, since appropriate chloramine concentrations were not available. It was not possible to estimate the proportion of TRC that was in the inorganic chloramine form. The use of TRC as a surrogate for inorganic chloramines meets the conservative objective of the assessment (McCullum *et al.*, 2000).

Industrial effluents were considered for the Tier 2 assessment; however, these data were not of as high quality as the municipal data. Industrial effluents were considered to be part of the same discharge category as municipal effluents, and the results from municipal facilities were assumed to be representative of industrial situations. Therefore, chloramine discharges from industrial facilities were considered to be equivalent in nature to chlorinated municipal wastewater discharges. One industrial discharge was modelled for the conservative assessment (the Clover Bar Generating Station cooling water discharge to the North Saskatchewan River at Edmonton, Alberta).

Results of the conservative assessment are presented in Tables 7 and 8, and these show that seven discharges (i.e., Rossdale WTP, E.L. Smith WTP, R.O. Pickard Environmental Centre, Saskatoon WWTP, Lethbridge WTP, Britannia WTP and Toronto Humber WWTP) produced quotients of 1–10, and four discharges (i.e., Ashbridges Bay WWTP, North Toronto WWTP, Okotoks WWTP and Clover Bar Generating Station) produced quotients of 10 or greater (McCullum *et al.*, 2000). The discharges resulting in quotients greater than 10 were recommended for a probabilistic risk assessment. In addition, the Rossdale WTP was recommended for a probabilistic risk assessment since its discharge resulted in the highest quotients from a water treatment facility waste. This discharge is also intermittent, and thus it is different from the continuous WWTP discharges but similar to those of the Clover Bar Generating Station.

Although other discharges produced risk quotients greater than one, the above discharges were considered to be representative of discharges that may produce ecological risk to aquatic biota in Canada. The above list includes wastewater

**Table 7** Summary of conservative assessment EECs and quotients for effluents and cooling water discharges to rivers and marine environments[1]

| Location | Approximate maximum EECs (mg/L) for distances (m) from source | | | | | | | Quotients (i.e., EEC + ENEV) for distances (m) from source | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 20 | 50 | 100 | 200 | 300 | 400 | 500 | 20 | 50 | 100 | 200 | 300 | 400 | 500 |
| **River discharges** | | | | | | | | | | | | | | |
| North Toronto WWTP – Don River | n/a | n/a | 0.746 | 0.595 | 0.567 | 0.547 | 0.521 | n/a | n/a | 133 | 106 | 101 | 98 | 93 |
| Okotoks WWTP – Sheep River | 0.292 | n/a | 0.159 | 0.115 | 0.095 | n/a | n/a | 52 | n/a | 28 | 21 | 17 | n/a | n/a |
| Edmonton Power, Clover Bar Generating Station – North Saskatchewan River | 0.855 | n/a | 0.601 | 0.524 | 0.468 | n/a | n/a | 153 | n/a | 107 | 94 | 84 | n/a | n/a |
| Edmonton Rossdale WTP – North Saskatchewan River | 0.050 | n/a | 0.031 | 0.026 | 0.022 | n/a | n/a | 9 | n/a | 6 | 5 | 4 | n/a | n/a |
| Edmonton E.L. Smith WTP – North Saskatchewan River | 0.039 | n/a | 0.024 | 0.020 | 0.017 | n/a | n/a | 7 | n/a | 4 | 4 | 3 | n/a | n/a |
| R.O. Pickard Environmental Centre – Ottawa River | n/a | n/a | 0.026 | 0.026 | 0.025 | 0.025 | 0.024 | n/a | n/a | 5 | 5 | 5 | 4 | 4 |
| Saskatoon WWTP – South Saskatchewan River | n/a | 0.018 | 0.013 | 0.010 | 0.010 | 0.010 | 0.010 | n/a | 3 | 2 | 2 | 2 | 2 | 2 |
| Lethbridge WTP – Oldman River | n/a | 0.021 | 0.011 | 0.008 | 0.007 | 0.006 | n/a | n/a | 4 | 2 | 1 | 1 | 1 | n/a |
| Britannia WTP – Ottawa River | n/a | 0.005 7 | 0.004 | 0.002 8 | 0.002 3 | 0.002 | 0.001 8 | n/a | 1 | 1 | 1 | 0.41 | 0.36 | 0.32 |
| Saskatoon WTP – South Saskatchewan River | n/a | 0.003 2 | 0.002 3 | 0.001 6 | 0.001 3 | 0.001 1 | n/a | n/a | 0.6 | 0.4 | 0.3 | 0.2 | 0.2 | n/a |
| Medicine Hat WWTP – South Saskatchewan River | n/a | 0.004 1 | 0.003 9 | 0.003 6 | 0.003 4 | 0.003 2 | 0.003 1 | n/a | 0.7 | 0.7 | 0.7 | 0.6 | 0.6 | 0.5 |
| Prince Albert WWTP – North Saskatchewan River | n/a | 0.002 7 | 0.001 9 | 0.001 3 | 0.001 1 | 0.000 9 | 0.000 8 | n/a | 0.5 | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 |
| Nelson WWTP – Kootenay River | 0.001 8 | n/a | 0.001 8 | 0.003 4 | 0.003 5 | n/a | n/a | 0.3 | n/a | 0.3 | 0.6 | 0.6 | n/a | n/a |
| Trail WWTP – Columbia River | 0.000 4 | n/a | 0.000 5 | 0.001 | 0.000 3 | n/a | n/a | 0.07 | n/a | 0.1 | 0.2 | 0.1 | n/a | n/a |
| **Marine discharges** | | | | | | | | | | | | | | |
| Charlottetown WWTP – Hillsborough River Estuary | n/a | 0.000 3 | 0.000 2 | 0.000 1 | 0.000 1 | 0.000 08 | 0.000 07 | n/a | 0.05 | 0.03 | 0.02 | 0.02 | 0.01 | 0.01 |
| Eastern Passage WWTP – Halifax Harbour | n/a | 0.000 5 | 0.000 4 | 0.000 3 | 0.000 2 | 0.000 2 | 0.000 1 | n/a | 0.09 | 0.07 | 0.05 | 0.04 | 0.03 | 0.02 |

[1] Source: McCullum *et al.* (2000).

**TABLE 8** Summary of conservative assessment EECs and quotients for effluents to Lake Ontario[1]

| Location | Approximate maximum EECs (mg/L) for distances (m) from source | | | | | Quotients (i.e., EEC ÷ ENEV) for distances (m) from source | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 100 | 250 | 500 | 750 | 1000 | 100 | 250 | 500 | 750 | 1000 |
| **Ashbridges Bay WWTP** | | | | | | | | | | |
| Perpendicular (to outlet) | 0.076 | 0.049 | 0.034 | 0.026 | 0.022 | 14 | 9 | 6 | 5 | 4 |
| Parallel | 0.046 | 0.020 | 0.0077 | 0.0038 | 0.002 | 8 | 3 | 1 | 0.7 | 0.4 |
| **Toronto Humber WWTP** | | | | | | | | | | |
| Perpendicular (to outlet) | 0.044 | 0.028 | 0.019 | 0.015 | 0.012 | 8 | 5 | 3 | 3 | 2 |
| Parallel | 0.027 | 0.011 | 0.004 | 0.002 | 0.001 | 5 | 2 | 0.7 | 0.4 | 0.2 |

[1] Source: McCullum *et al.* (2000).

effluents, a WTP waste discharge and a cooling water discharge. Although no existing marine or estuarine discharge scenarios were recommended for Tier 3, this does not mean that new discharges to marine or estuarine environments could not produce negative ecological consequences. As shown in the toxicity assessment (Farrell and Wan, 2000), saltwater biota are very sensitive to residual oxidant exposures resulting from chloramine releases. In the event that a facility discharging chloramines were proposed, risk assessment methods such as those used in this PSL assessment should be used to ensure that discharges do not result in unacceptable ecological risk.

Conservative assessment of chloramine exposure from potable water

The purpose of the conservative assessment of chloramine exposure from potable water sources was to determine types of releases that may produce risk and to generate data that could be useful (if necessary) for risk management. A generic evaluation of drinking water was conducted using a simple dilution and decay model for streams having discharges ≤1.0 $m^3/s$ and mixing models for larger surface waters, including streams with discharges >1.0 $m^3/s$, as well as lake and marine environments. This assessment was intended to serve as a management tool, with the focus being on identification of potential impacts resulting from discharges having different flow rates, chloramine concentrations and rates of decay. Models were used to estimate chloramine concentrations in water under various simplified discharge scenarios. Actual discharge events could not be modelled due to an absence of data pertaining to stream and drinking water flow rates, chloramine concentrations and *in situ* chloramine decay rates.

To simplify the assessment, chloraminated water releases were classified into the following flow rates: 0.0001, 0.001, 0.01, 0.1 and 1 $m^3/s$. These represent a broad spectrum of discharges, from a small leak (0.0001 $m^3/s$) to a very severe main break (1 $m^3/s$). Also, data regarding chloramine concentrations, stream discharge and decay rates were selected to represent three geographically and climatically diverse case study locations: Abbotsford and Mission (coastal British Columbia), Edmonton (Prairie region) and Brantford (Great Lakes region). Rates of chloramine decay identified in the open literature and derived using water from each region were selected. This resulted in decay rate constants that represented high-demand (20 per day, half-life of 0.03 days; Prairie region), medium-demand (4.97 per day, half-life of 0.14 days; Great Lakes region) and low-demand (0.734 per day, half-life of 0.94 days; coastal British Columbia) scenarios (Wisz *et al.*, 1978; Milne, 1991; Norecol Environmental Consultants Ltd. and Dayton and Knight Ltd., 1993). For each region, high and low chloramine concentrations in their potable water supply reported by the three case study municipalities were used.

A small stream model was used to estimate EECs in streams with different discharge rates (0.001, 0.01, 0.1 and 1 $m^3/s$). Mixing models derived by the University of Alberta were also used to determine chloramine fate and EECs in larger water bodies (Fraser River, North Saskatchewan River and Grand River) and in a generic lake and marine environment. EECs were compared with ENEVs for fresh water and salt water, and risk quotients were determined. No-effect values for short-term (8 hours, 0.015 mg/L) and long-term (17.9 hours, 0.0056 mg/L) chloramine exposures were compared with the EECs.

For small streams, results of the conservative assessment were summarized as dilution ratios relating to the approximate drinking water discharge rates that result in EECs that exceed the ENEV. Assuming direct discharge of potable water to a surface water, the results suggest that:

- In Mission and Abbotsford, short-duration (i.e., 8 hours) drinking water discharges containing 0.2 mg chloramine/L could impact on a small stream if diluted with surface water by a ratio of less than 1:10. A discharge with 1.020 mg chloramine/L could impact on

a small stream if diluted with surface water by a ratio of less than 1:100 to 1:10. Long-duration discharges (≥17.9 hours) could impact on a small stream if diluted with surface water by a ratio of less than 1:100 to 1:10.

- In Edmonton and Brantford, Ontario, a short-duration discharge of 1.030–2.400 mg chloramine/L may produce impacts in a small stream when diluted with surface water by a ratio of less than 1:100. A long-term discharge with concentrations of 1.030–2.400 mg/L could produce impacts when diluted by a ratio of approximately less than 1:1000 to 1:100.

In reality, most discharges of chloraminated drinking water to surface waters would be indirect and would travel overland or through storm sewers prior to entering a surface water. This assessment suggests that pathways that have sufficiently high chemical decay and that are sufficiently long could decrease chloramine concentrations to levels that do not result in impacts to surface waters. A high-demand pathway may result from exposure to biological materials such as slimes and fungi and entrainment with high levels of suspended sediments containing various oxidizable organic substances. Soil infiltration and evaporation would influence losses en route to the surface waters. On the other hand, pathways not exposed to organic materials, without significant losses due to infiltration and evaporation, would not result in large chloramine losses. Drinking water releases occur from several sources, including distribution system leaks and breaks, lawn and garden watering, car and driveway washing, street cleaning, main flushing, fire fighting and relevant training, as well as industrial or commercial washdown and construction activities. These uses occur predominantly on land; hence, flows produced by these activities would usually incur some decay en route to a surface water.

The generic modelling indicated that a chloraminated flow of potable water from a typical garden hose could result in some marginal impacts if the discharge were direct to a very small stream and if decay was sufficiently slow. However, most flows of this nature are indirect. Environmental sampling conducted in the FVRD (i.e., Vanden Berg and Wade, 1997; Pasternak *et al.*, 1998, 1999) could not detect measurable concentrations of chloramines in surface waters from indirect sources such as water used for lawn watering and equipment washdowns. These studies show that common indirect small flows with magnitudes of approximately ≤0.001 $m^3/s$ would not result in impacts to surface waters.

Larger flows with discharges of ≥0.01 $m^3/s$, such as from large distribution system leaks, main breaks, fire hose discharges, main flushing, street washing and some industrial and commercial activities, may have a greater possibility of producing impacts. Direct discharges of approximately 0.01 $m^3/s$ and greater may potentially have an impact on small streams with discharges of approximately ≤0.1 $m^3/s$ in Abbotsford and Mission and streams with discharges of ≤1.0 $m^3/s$ in Edmonton and Brantford. Impacts may be greater near to the source of discharged water in Edmonton and Brantford, since chloramine concentrations in drinking water are reportedly higher in these municipalities than in Abbotsford and Mission. However, impacts may be localized in Edmonton and Brantford due to the presumed faster rate of chloramine decay. A summary of potable water flow rates that could impact on larger surface waters has been included in Table 9.

The Tier 2 assessment found that the greatest total number of accidental releases of chloraminated potable water occurred in the City of Edmonton (627 in 1996, 780 in 1995), followed by the City of Brantford (45 in 1996, 50 in 1995) and Mission/Abbotsford (7 in 1996 and 1997, 22 in 1994). In 1996, the regional water service area for Edmonton repaired one break per leak for approximately each 3.7 km of distribution main. In Brantford and Mission/Abbotsford, approximately one break per leak was repaired for each 8.5 and 45.7 km of distribution main, respectively, during 1996 (Pasternak, 2000). Although a larger number of drinking water releases occurred in Edmonton and Brantford,

**TABLE 9** Summary of approximate drinking water discharges ($m^3/s$) that may result in impacts to large surface waters[1]

| Surface water | Drinking water discharges ($m^3/s$) | | | |
|---|---|---|---|---|
| | Short exposure[2] | | Long exposure[3] | |
| | Low chloramine concentration[4] | High chloramine concentration[5] | Low chloramine concentration[4] | High chloramine concentration[5] |
| Fraser River | ≥1 | ≥1 | ≥1 | ≥0.1 |
| North Saskatchewan River | ≥0.1 | ≥0.1 | ≥0.1 | ≥0.1 |
| Grand River | ≥0.01 | ≥0.01 | ≥0.01 | ≥0.001 |
| Lake | ≥0.1 | ≥0.1 | ≥0.1 | ≥0.01 |
| Marine | ≥1 | ≥1 | ≥1 | ≥1 |

[1] Source: Pasternak (2000).

[2] Used 8-hour exposure.

[3] Used 17.9-hour exposure.

[4] Used minimum chloramine concentrations in drinking water reported by Mission/Abbotsford, British Columbia (0.2 mg/L), Edmonton, Alberta (1.03 mg/L), and Brantford, Ontario (1.6 mg/L), for simulations in Fraser River, North Saskatchewan River and Grand River, respectively. The national average minimum (0.61 mg/L) was used for the generic simulations of lake and coastal environments.

[5] Used maximum chloramine concentrations in drinking water reported by Mission/Abbotsford, British Columbia (1.02 mg/L), Edmonton, Alberta (2.36 mg/L), and Brantford, Ontario (2.4 mg/L), for simulations in Fraser River, North Saskatchewan River and Grand River, respectively. The national average maximum (1.56 mg/L) was used for the generic simulations of lake and coastal environments.

this does not necessarily mean that the greatest risk to aquatic biota occurs in these regions. The proximity and frequency of small streams with sensitive habitat and significant fish resources, destination of storm sewer discharge, as well as the number and magnitude of accidental chloramine releases are important factors affecting risk to aquatic biota.

In 1996, Edmonton and Brantford did not have a high topographical frequency of small streams, and a lower proportion of drinking water releases occurred in close proximity to their surface waters. Overall, the approximate average distance of a main break to a local surface water (named or unnamed) was approximately 180 m in Mission/Abbotsford and approximately 1200 m in both Edmonton and Brantford (Pasternak, 2000).

Data on the proportion of larger potable water discharges that flow to a surface water are not available; however, some indication of destination is suggested by the design of storm sewers. In Mission and Abbotsford, as well as in Brantford, storm sewers lead to local surface waters, ditches or retention areas. Sanitary sewers are not designed to capture surface water drainage in Brantford, Mission or Abbotsford (District of Mission, 1979; Eldridge, 1999). In Edmonton, approximately 75% of storm sewers flow to the North Saskatchewan River, while the remaining 25% are combined sanitary/storm sewers leading to the WWTP (Environment Canada, 1997b).

In Mission and Abbotsford, due to the abundance of streams in the area, overland and storm sewer pathways to these surface waters can be short. In other regions, the occurrence of small streams is less frequent; therefore, there are often greater distances to travel overland or via storm drains to surface waters. Particularly in the Prairie and Great Lakes regions, chloramine decay presented by long overland or storm sewer pathways and the high dilution resulting from the destination surface water may act to mitigate chloramine impacts.

**TABLE 10** Characterization of main breaks and release of chloraminated potable water to Fergus Creek, British Columbia[1]

| Date of spill | Description of main | Estimated volume released ($m^3$) | Discharge rate ($m^3/s$) | Duration (min) | Chloramine concentration (mg/L as TRC)[2] |
|---|---|---|---|---|---|
| 17 October 1989 | 8" main | 330 | 0.183 | 30 | 2.53 |
| 9 July 1990 | aged concrete – asbestos | 23 000 | 1.6–2.1 | 180–240 | 2.75 |

[1] Source: Nikl and Nikl (1992).

[2] Chloramine concentration measured in potable water. Samples taken at locations along distribution system near the breaks.

Other evidence of risk due to accidental releases of potable water

High ecological impact from accidental releases of potable water to small streams has been established. Two events, occurring on October 17, 1989, and July 9, 1990, in Surrey, British Columbia, resulted in devastating consequences to Fergus Creek (Table 10). Both events resulted in convictions under the *Fisheries Act*. Inorganic chloramine was identified as the culprit responsible for impacts (Nikl and Nikl, 1992). These main breaks occurred during a pilot study designed to determine the feasibility of chloramination for secondary treatment of drinking water in the Greater Vancouver Regional District.

Fergus Creek is a small stream for which discharge monitoring data do not exist; however, it has been estimated to have an average base flow rate of 0.065–0.130 $m^3/s$. The stream is approximately 6 km long and flows from its headwaters in an agricultural area into the Little Campbell River. The lower 1.5 km of Fergus Creek support significant salmon habitat.

The first event released treated water that flowed approximately 1 km over lawns and through ditches and a storm drain to Fergus Creek and en route entrained large amounts of highly organic sediment. Eyewitnesses reported seeing fish attempting to leap out of the water, thereby suggesting a vigorous avoidance reaction by the fish. After the 30-minute spill, an estimated 1700–2000 juvenile coho salmon and lesser numbers of cutthroat trout (*Oncorhynchus clarki*) carcasses were observed along Fergus Creek downstream of the point of toxicant entry into the stream. Upstream of the point of entry, live juvenile coho salmon were abundant. No dead fish were observed in the Little Campbell River (Nikl and Nikl, 1992).

Flow from the second event travelled a short distance overland into the headwaters of Fergus Creek. The treated water then flowed for 4.5 km in Fergus Creek before entering the area of the stream containing fish habitat. The break resulted in an estimated 3000 fish carcasses of predominantly juvenile coho salmon. Throughout Fergus Creek, the stream bed was covered in dead stream insects and other invertebrates (Nikl and Nikl, 1992).

The results of the conservative assessment and evidence from actual events provide sufficient rationale to further the assessment of potable water to a probabilistic level. However, there is an absence of comprehensive data pertaining to potable water releases, particularly those that are accidental in nature. This absence seems to be due to their unpredictable nature.

All accounts of ecological impact resulting from chloramine-treated potable water releases are in the Lower Mainland area of British Columbia. There are no documented reports

of impacts occurring from chloramine-treated potable water releases in any other region of Canada. The available information suggests that this is due to the high frequency of small streams with high water quality in the Lower Mainland of British Columbia.

#### *3.1.2.2.3 Probabilistic assessment of chloramine exposure from effluents and cooling water*

Receptors and assessment endpoints

The probabilistic risk assessment was focused on sensitive invertebrate and fish species commonly found in Canada. Sensitive receptors included the freshwater invertebrate, *C. dubia*, and a juvenile freshwater life stage of the anadromous fish, chinook salmon. The chinook salmon was chosen as a fish receptor, although this species was not found to be the most sensitive freshwater fish species, and in spite of the fact that it is not ubiquitous across Canada. However, it is related to other salmonid species, such as rainbow trout and coho salmon, which have a similar or greater sensitivity to chloramines, and together, salmonids are widely distributed throughout Canada (Scott and Crossman, 1973). As indicated in Section 2.4.2.3, coho salmon was found to be the most sensitive species to chloramine exposure (96-hour $LC_{50}$ = 0.07 mg/L).

To estimate risks of exposures of aquatic biota to chloramine, each exposure distribution was compared with three incipient lethality endpoints: 50% mortality to *C. dubia* (0.018 mg/L); and 50% (0.112 mg/L) and 20% (0.077 mg/L) mortality to chinook salmon. The probability that exposures exceed the endpoints was calculated. Each effect endpoint was modelled using time-series data so that the threshold concentration could be determined beyond which longer durations produced no additional mortality (incipient lethality) for *C. dubia* and little additional mortality (7-day $LC_{50}$) for chinook salmon. The details of this analysis are in Farrell and Wan (2000: Appendices B, C and H).

To bound risk estimates, months were selected that resulted in a high or a low risk to sensitive receptors. Selecting high- and low-risk months was difficult because aquatic biota are sensitive to chloramines at many life stages and acute lethality occurs at very low concentrations (Farrell and Wan, 2000: Appendix A). Each case study included specific months that were selected based on professional judgment, release patterns and organism life history. As will be discussed in the following paragraphs, limitations in the available hydrological and effluent data precluded an assessment for a portion of the selected months.

Probabilistic risk assessment of effluents and cooling water

McCullum *et al.* (2000) recommended that probabilistic risk assessments be conducted for chloramine releases from the Ashbridges Bay WWTP, North Toronto WWTP, Okotoks WWTP, Clover Bar Generating Station and Rossdale WTP. Although other discharges produced risk quotients greater than one, the above discharges were considered to be representative of discharges that may produce ecological risk to aquatic biota in Canada. The above list includes wastewater effluents, a WTP waste discharge and a cooling water discharge.

Inadequate hydrological data were available for a Tier 3 assessment of aquatic biota exposed to chloramines in the Sheep River near the Okotoks WWTP; hence, a probabilistic risk assessment could not be conducted for this discharge. However, a cursory analysis of the available data found that discharges from the Okotoks WWTP to the Sheep River and from the North Toronto WWTP to the Don River are similar. Both effluents are released to a small-sized and shallow river. However, the effluent from the North Toronto WWTP received less dilution than the discharge from the Okotoks WWTP; thus, one would expect a higher risk to biota from the Toronto facility. In 1996, discharge from the Okotoks WWTP contained an average TRC concentration of 3.0 mg/L and had an

average flow rate of 3218 $m^3/d$. The 20-year estimated mean (arithmetic, 1976–1995) flow rate for the Sheep River was 1 209 600 $m^3/d$ (Environment Canada, 1997b, 1999a). In 1998, Golder Associates Ltd. undertook sampling in the Sheep River and found measurable levels of CRC (mean 0.03 mg/L) close to the north bank up to 150 m downstream from the Okotoks WWTP (Golder Associates Ltd., 1998). These data are also described by Pasternak and Powell (2000). In 1996, discharge from the North Toronto WWTP contained an average TRC concentration of 1.6 mg/L and had an average flow rate of 33 528 $m^3/d$. The estimated 20-year mean (arithmetic, 1976–1995) flow rate for the Don River was 226 400 $m^3/d$ (Environment Canada, 1997b, 1999a).

Discharges from the Rossdale WTP to the North Saskatchewan River are small (0.1–0.2 $m^3/s$), intermittent and of short duration (typically 30 minutes). Such discharges require a "slug" model to estimate plume concentrations and plume duration. Although such models exist, their performance at predicting concentrations in the receiving environment was found to be poor. Furthermore, the risks from this source are likely to be much smaller than those from the Clover Bar Generating Station. The latter has larger discharges (21.2 $m^3/s$) of longer duration (typically 4–24 hours) to the same river with approximately the same chlorine residual concentration in the effluent (0.3–1 mg/L). For these reasons, the Rossdale WTP case study was not pursued any further.

To characterize annual variation in exposure to inorganic chloramines, the Tier 3 assessment was conducted using effluent and hydrological data spanning 4 years. Longer time periods were not selected due to limitations in the available historic data and because many wastewater facilities have changed processes in recent years in an effort to improve effluent quality.

A river mixing model was used to predict downstream chloramine concentrations on a spatial grid in the North Saskatchewan River (and Don River case studies. A lake mixing model was used in the Lake Ontario case study. The equations for both models are described in McCullum *et al.* (2000).

The river mixing model assumes complete vertical mixing of the effluent plume and thus is a two-dimensional mass transport model. The assumption of instantaneous mixing may not be realistic under certain circumstances. For instance, layering may occur if the temperatures in effluent and receiving water are sufficiently different and if the discharge outlet does not result in effluent diffusion. In such circumstances, the model would underestimate risks due to chloramine exposure. The river channel is assumed to be rectangular, and distance coordinates are in dimensionless form for both the longitudinal and lateral directions. The model accounts for a channel of confined width, with concentration reflection occurring. Further, the model has been modified to take account of instantaneous chlorine demand and decay following release.

Parallel shore currents tend to dominate flow patterns in large lakes within a few kilometres of the shore. These currents have the capacity to transport and disperse effluents that have been discharged near the shoreline. For the Lake Ontario case study, we used a lake mixing model that assumed steady parallel shore currents and a continuous effluent source. This model also assumed a constant depth and near-instantaneous vertical mixing. As with the river mixing model, the lake mixing model was modified to account for instantaneous chlorine demand and chloramine decay following release.

In order to run the models, hydrometric, dispersion, chloramine decay and effluent data were gathered and summarized in a manner appropriate for use with the selected models for each of the case studies (see Moore *et al.*, 2000).

Distributions of exposure were generated by Monte Carlo analysis using river and lake models (Table 11). The model equations are described by McCullum *et al.* (2000). The

**TABLE 11** Input distributions and point estimates used in case studies for probabilistic risk assessment[1]

| Variable | Distribution | Month | Parameters |
|---|---|---|---|
| **Clover Bar Generating Station – North Saskatchewan River** | | | |
| Discharge location | Point estimate | August | 0.98 |
| Initial chlorine demand | Point estimate | August | 0.44 |
| Velocity (m/s) | Point estimate | August | 0.73 |
| Effluent flow ($m^3/s$) | Point estimate | August | 21.2 |
| Effluent concentration (mg/L) | Lognormal | August | Mean = 0.68, s = 0.10, $r_{effluent\ decay}$ = –0.64 |
| Stream flow ($m^3/s$) | Lognormal | August | Mean = 208.1, s = 51.8 |
| Transverse mixing coefficient ($m^2/s$) | Lognormal | August | Mean = 0.09, 50%ile = 0.07, 90%ile = 0.34 |
| Decay rate constant (/d) | Lognormal | August | Mean = 67.96, s = 62.88, $r_{effluent\ decay}$ = –0.64 |
| Depth (m) | Normal | August | Mean = 1.90, s = 0.30 |
| Width (m) | Normal | August | Mean = 150, s = 10 |
| **Don River** | | | |
| Effluent concentration (mg/L) | Lognormal | January | Mean = 1.27, s = 0.36, $r_{effluent\ decay}$ = –0.64 |
| | | March | Mean = 1.31, s = 0.40, $r_{effluent\ decay}$ = –0.64 |
| | | August | Mean = 1.23, s = 0.40, $r_{effluent\ decay}$ = –0.64 |
| | | October | Mean = 1.15, s = 0.46, $r_{effluent\ decay}$ = –0.64 |
| Effluent flow ($m^3/s$) | Lognormal | January | Mean = 0.42, s = 0.01 |
| | | March | Mean = 0.42, s = 0.02 |
| | | August | Mean = 0.37, s = 0.08 |
| | | October | Mean = 0.40, s = 0.02 |
| Stream flow ($m^3/s$) | Lognormal | January | Mean = 5.51, s = 2.66 |
| | | March | Mean = 5.59, s = 1.47 |
| | | August | Mean = 3.55, s = 0.63 |
| | | October | Mean = 3.33, s = 1.67 |
| Transverse mixing coefficient ($m^2/s$) | Lognormal | January | Mean = 0.01, s = 0.01 |
| | | March | Mean = 0.01, s = 0.01 |
| | | August | Mean = 0.01, s = 0.01 |
| | | October | Mean = 0.01, s = 0.01 |
| Decay rate constant (/d) | Lognormal | January | Mean = 2.64, s = 2.44, $r_{effluent\ decay}$ = –0.64 |
| | | March | Mean = 2.64, s = 2.44, $r_{effluent\ decay}$ = –0.64 |
| | | August | Mean = 67.96, s = 62.88, $r_{effluent\ decay}$ = –0.64 |
| | | October | Mean = 35.30, s = 32.66, $r_{effluent\ decay}$ = –0.64 |
| Width (m) | Point estimate | January | 20.6 |
| | Point estimate | March | 20.5 |
| | Normal | August | Mean = 20.53, s = 0.64 |
| | Normal | October | Mean = 20.33, s = 0.29 |
| Velocity (m/s) | Point estimate | January | 0.47 |
| | Point estimate | March | 0.33 |
| | Lognormal | August | Mean = 0.22, s = 0.06 |
| | Lognormal | October | Mean = 0.21, s = 0.02 |
| Depth (m) | Point estimate | January | 0.45 |
| | | March | 0.45 |
| | | August | 0.45 |
| | | October | 0.45 |
| Discharge location (0.5 centre, 0 & 1 bank) | Point estimate | January | 0.8 |
| | | March | 0.8 |
| | | August | 0.8 |
| | | October | 0.8 |

**TABLE 11** (continued)

| Variable | Distribution | Month | Parameters |
|---|---|---|---|
| Initial chlorine demand | Point estimate | January | 0.44 |
| | | March | 0.44 |
| | | August | 0.44 |
| | | October | 0.44 |
| **Lake Ontario** | | | |
| Effluent concentration (mg/L) | Lognormal | January | Mean = 1.10, s = 0.21, $r_{effluent\ decay}$ = –0.64 |
| | | April | Mean = 0.98, s = 0.24, $r_{effluent\ decay}$ = –0.64 |
| | | July | Mean = 1.02, s = 0.19, $r_{effluent\ decay}$ = –0.64 |
| | | October | Mean = 1.04, s = 0.22, $r_{effluent\ decay}$ = –0.64 |
| Effluent flow ($m^3/s$) | Lognormal | January | Mean = 8.62, s = 0.84 |
| | | April | Mean = 8.14, s = 0.48 |
| | | July | Mean = 7.85, s = 0.39 |
| | | October | Mean = 7.72, s = 0.43 |
| Decay rate constant (/d) | Lognormal | January | Mean = 35.30, s = 32.66, $r_{effluent\ decay}$ = –0.64 |
| | | April | Mean = 35.30, s = 32.66, $r_{effluent\ decay}$ = –0.64 |
| | | July | Mean = 35.30, s = 32.66, $r_{effluent\ decay}$ = –0.64 |
| | | October | Mean = 35.30, s = 32.66, $r_{effluent\ decay}$ = –0.64 |
| Width of lake (m) | Point estimate | January | 50 000 |
| | | April | 50 000 |
| | | July | 50 000 |
| | | October | 50 000 |
| Depth of mixing layer (m) | Point estimate | January | 3 |
| | | April | 3 |
| | | July | 3 |
| | | October | 3 |
| Velocity along the shoreline (m/s) | Point estimate | January | 0.12 |
| | | April | 0.12 |
| | | July | 0.12 |
| | | October | 0.12 |
| Longitudinal dispersion coefficient ($m^2/s$) | Point estimate | January | 50 |
| | | April | 50 |
| | | July | 50 |
| | | October | 50 |
| Lateral dispersion coefficient ($m^2/s$) | Point estimate | January | 0.2 |
| | | April | 0.2 |
| | | July | 0.2 |
| | | October | 0.2 |
| Initial chlorine demand | Point estimate | January | 0.85 |
| | | April | 0.85 |
| | | July | 0.85 |
| | | October | 0.85 |

[1] Source: Moore *et al.* (2000).

technique involved defining distributions to each variable used by the environmental fate models. The models used input values selected from each of the distributions. By running the models, output exposure values were generated. The Monte Carlo analysis involved repeating this process 10 000 times to generate a distribution of output values. For each case study site, separate analyses were conducted and exposure distributions were produced for locations on a grid near the effluent outfall. These analyses were repeated for different months for the Don River and Lake Ontario case studies. The Monte Carlo analysis was conducted using Crystal Ball, version 4.01. Using Monte Carlo simulation, Crystal Ball forecasts the range of possible results for a given situation, thereby allowing estimation of the likelihood of an event occurring. For complete details regarding the methodology used, consult Moore *et al.* (2000).

***Don River***: Probabilistic risk assessments were conducted for the Don River for the months of January, March, August and October. The results indicated that risks were greatest in January and lowest in August (Figure 8a–h). In January, risks to *C. dubia* are severe, with probabilities >80% for 50% or greater mortality for over half the width of the river at the greatest distance from the outfall modelled in this case study (1900 m) (Figure 8a,b). Farther downstream, the Don River discharges into Lake Ontario. By August, chloramine risks to *C. dubia* are much reduced, with probabilities <10% for 50% mortality or greater for the entire width of the river 1800 m from the outfall (Figure 8c,d). The risks in October are intermediate between those observed in January and August.

In January and March, chloramine risks to sensitive life stages of chinook salmon are moderate, with probabilities of up to 41% for 20% mortality 1900 m from the outfall (Figure 8e,f). By August, risks to salmon have decreased (Figure 8g,h), with probabilities of up to approximately 20% for 20% mortality 600 m from the outfall.

Sensitivity analyses from the January analyses indicated that the most important input variables influencing chloramine concentrations at the left bank (0 m, shore opposite from the discharge) were the transverse mixing coefficient initially (correlation coefficient or $r > 0.5$ up to 900 m from the outfall) and the effluent concentration ($r > 0.5$) and decay rate ($r > -0.7$) farther downstream.

The largest seasonal variation in input variables was observed with hydrological and decay parameters (see Table 12); thus, seasonal differences in risk may be attributed largely to these variables. The modelling exercise made use of discharge rates for the Don River, which varied from 3.3 $m^3/s$ for October to 5.6 $m^3/s$ for March, and decay rates ranging from 2.64 per day for January and March to 35.5 per day for October and 67.98 per day for August. If all model input variables were seasonally constant except for the river discharge rate, seasonal differences in EEC and risk would be proportional to variations in river discharge rates. The highest risk to aquatic biota would occur during the period of minimal dilution (i.e., during the summer and fall), and the lowest risk would occur during the months with the highest dilution (i.e., during the winter and spring). However, chloramine EEC decreases very rapidly during the months of August and October due to the estimated rapid rates of chloramine decay. The overall net effect of dilution and decay in this scenario is that risk is lowest during the summer months when decay is highest, in spite of the fact that discharge is lower than that experienced during other months of the year. The risk to aquatic biota is highest during winter and early spring when rates of decay are estimated to be very low, in spite of the fact that dilution of the effluent is highest at this time of the year.

A limited number of samples were taken from the Don River in August–September 1998 to determine chloramine levels. The levels found 200 m (<0.005–0.013 mg/L) and 500 m (<0.005 mg/L) downstream along the shore closest to the outfall side were within factors

**FIGURE 8** Spatial distribution of risk for *Ceriodaphnia dubia* (Cd) and *Oncorhynchus tshawytscha* (Ot) exposed to inorganic chloramines discharged by the North Toronto WWTP to the Don River: (a) and (b) January – Cd; (c) and (d) August – Cd; (e) and (f) January – Ot; and (g) and (h) August – Ot (Moore *et al.*, 2000)

Figure 8a

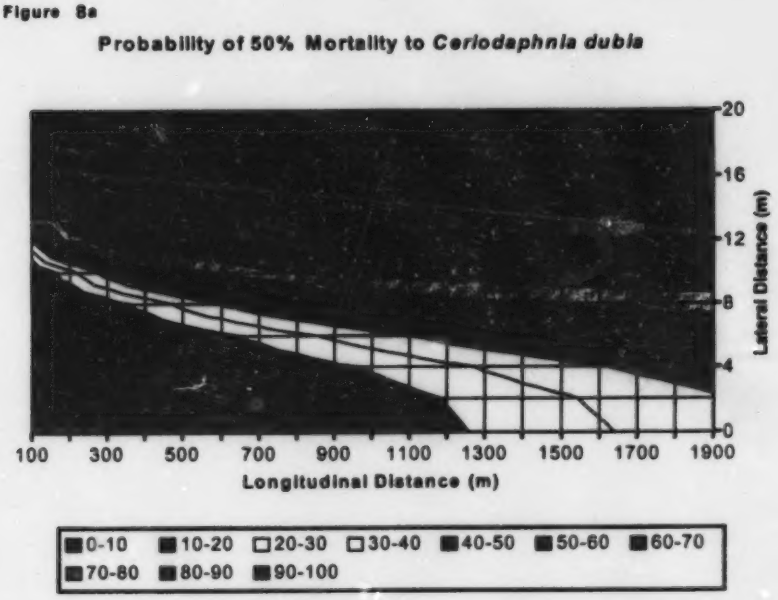
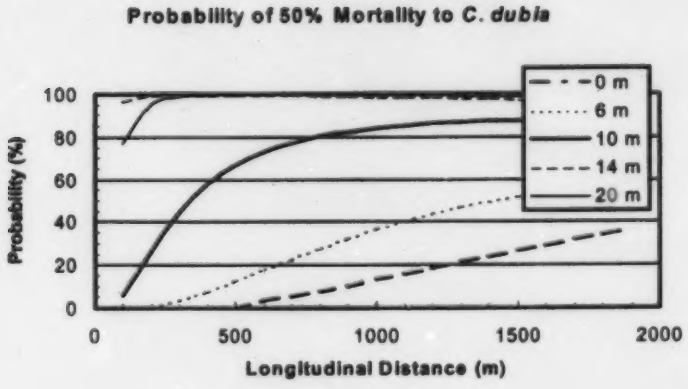



Figure 8b

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of 5 and 2, respectively, of the 50th percentile concentrations predicted by the river model. Both values were within the output distributions predicted by the model. All other samples at these distances had levels below the analytical detection limit (0.005 mg/L), results that also correspond reasonably well with model predictions.

***Lake Ontario (Ashbridges Bay)***: The risk analyses for Lake Ontario were done for the

FIGURE 8 (continued)

Figure 8c

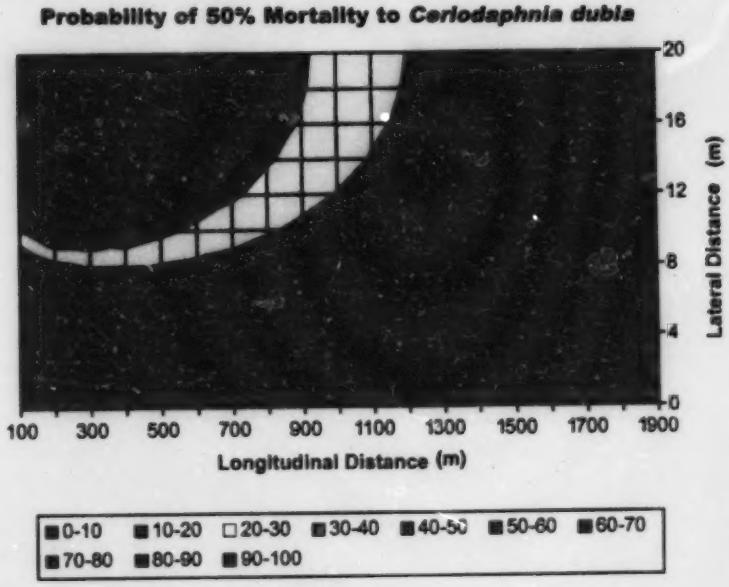
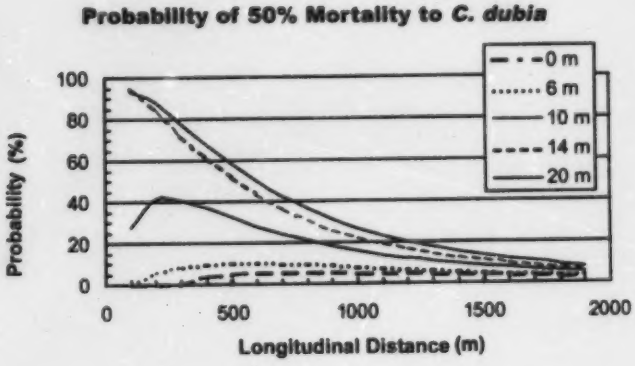



Figure 8d

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months of January, April, July and October. The results, however, indicated very little temporal variation in the estimated chloramine concentrations and hence risk. Risks to *C. dubia* and chinook salmon are highest by a marginal level in January. These January results are graphically depicted in Figure 9. This result is likely due to the lack of variation in the input variables for effluent concentration, effluent flow rate and decay rate. The results for all months indicate that the probabilities of 50% or greater mortality to *C. dubia* are fairly high (>40%) only in a narrow band (–250 m to +250 m) that runs parallel to the shoreline over a longitudinal distance of approximately 2000 m (Figure 9a,b). Probabilities of 20% or greater mortality to early

FIGURE 8 (continued)

Figure 8e

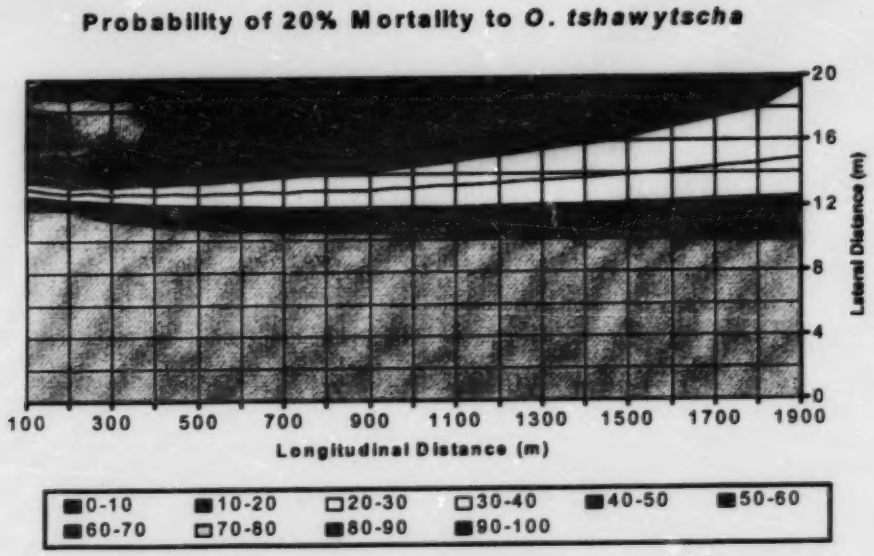
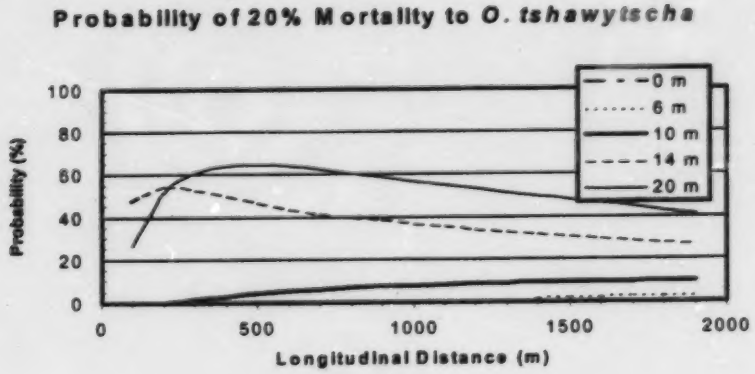



Figure 8f

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life stages of chinook salmon are low even close to the outfall (Figure 9c,d).

The lake model assumed complete and instantaneous mixing over the entire depth of the mixing layer (near the shore, this is assumed to equal the depth of the lake). Since the average depth of the lake in the vicinity of the discharge was determined to be approximately 3 m, this indicates the importance of rapid dilution as a factor affecting chloramine EECs.

***North Saskatchewan River***: The risk analyses of chloramines discharged from the Clover Bar Generating Station to the North Saskatchewan River were run only for the month

**FIGURE 8** (continued)

Figure 8g

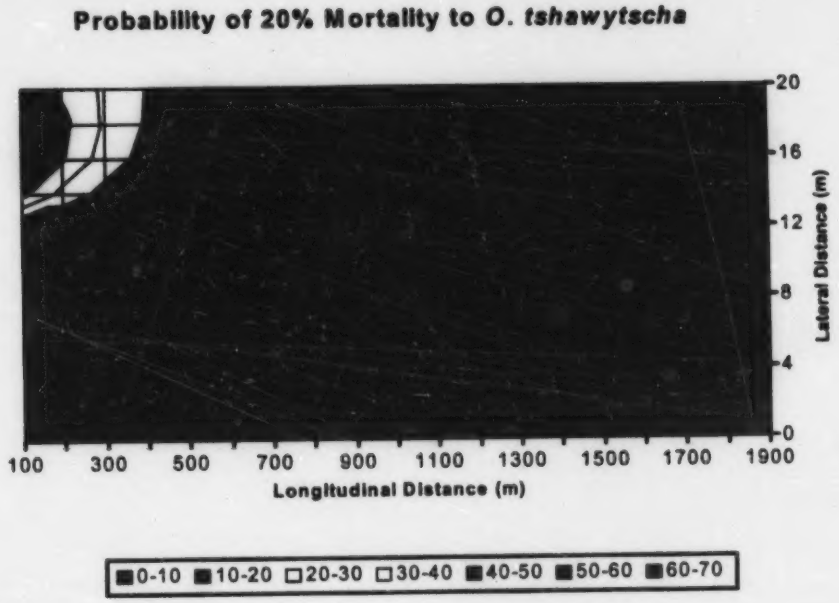
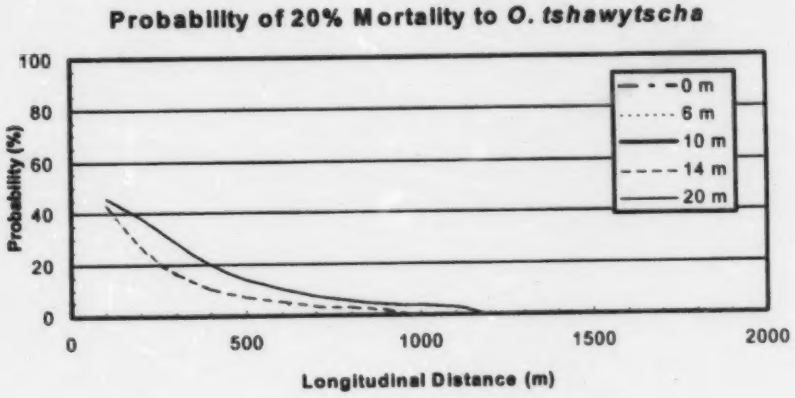



Figure 8h




of August, because of data limitations for other months of the year for stream flow, river width, river depth and cooling water discharge rates and concentrations. For August, we were able to obtain approximately 20 years of data for the stream flow, river width and river depth variables from the supporting document for the Priority Substances List assessment on ammonia (Environment Canada, 2000). Dilution is at its lowest in the North Saskatchewan River in August, thus making this time of year a potentially high-risk scenario.

The Clover Bar Generating Station releases chloramines intermittently for periods ranging from several hours to just over a day. Because incipient lethality for *C. dubia* is reached in approximately this time frame, we used a

**FIGURE 9** Spatial distribution of risk for *Ceriodaphnia dubia* (Cd) and *Oncorhynchus tshawytscha* (Ot) exposed to inorganic chloramines discharged by Ashbridges Bay WWTP to Ashbridges Bay, Lake Ontario: (a) and (b) January – Cd; (c) and (d) January – Ot (Moore *et al.*, 2000)

Figure 9a

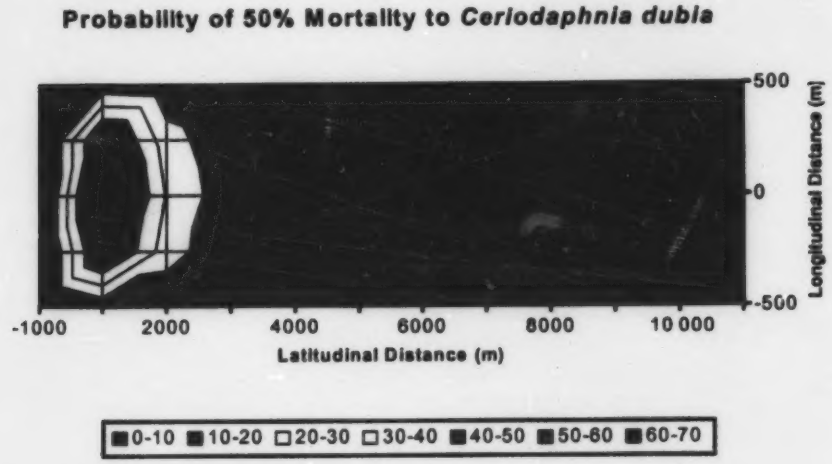
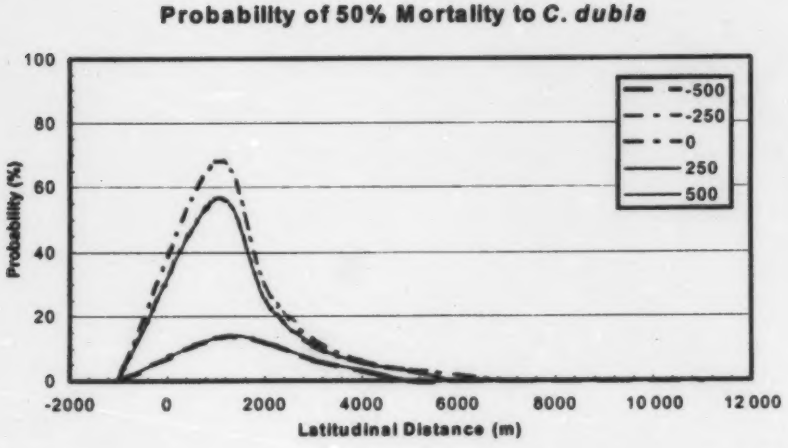



Figure 9b

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continuous-release model to simulate exposures, rather than a slug release model that we found performed very poorly.

The analyses indicated that the plume from the Clover Bar Generating Station was narrow and remained close to the shoreline on the outfall side (Figure 10a–f). Except for a band approximately 45 m wide and 6500 m long, probabilities of 50% or greater mortality to *C. dubia* were <10% (Figure 10a,b). Risks were fairly high (>40% probability of 50% or greater mortality) in an area approximately 30 m wide and up to 3000 m downstream of the outfall. Risks to early life stages of chinook salmon were very low.

**FIGURE 9** (continued)

Figure 9c

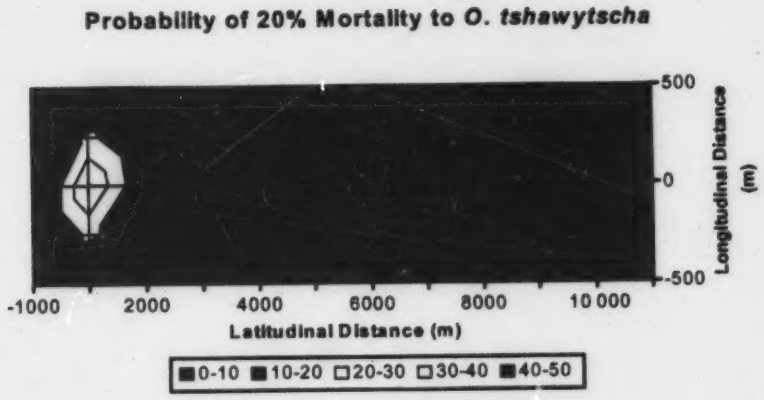
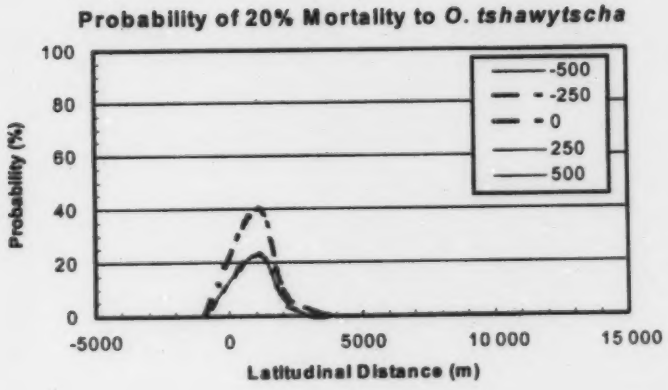



Figure 9d




## Conclusions

In the Don River, forecasted risks were most severe in January, with probabilities of >80% for 50% or greater mortality for *C. dubia* at 1900 m from the source. Lowest risk was forecasted for the month of August, with probabilities of up to 41% for 20% mortality at 1900 m from the outfall. For Lake Ontario in January, there was a probability of 2–68% for 50% mortality to *C. dubia* in a narrow, semi-elliptical band that was at least 500 m in width and extended approximately 6000 m. In July, the lowest risk was forecasted (range of 3–63% probability for 50% mortality in the zone 500 m in width and 4000 m in length). In the North Saskatchewan River, it appeared that elevated risk (i.e., >40% probability of 50% or greater mortality to *C. dubia*) was contained in a plume stretching to a maximum 30 m wide and approximately 3000 m long.

Since fish are less sensitive to chloramine than invertebrates, probabilities of risk to chinook

**TABLE 12** Months identified for probabilistic assessment for each case study based on receptor life history and water body hydrology

| Site | Invertebrates[1] | | Chinook salmon[2] | | | |
|---|---|---|---|---|---|---|
| | Low risk | High risk | Spring | Summer | Fall | Winter |
| Don River at Todmorden | August | October | March[3] | June | October | January[4] |
| Sheep River at Okotoks | June[3] | October[4] | March | June[3] | October[4] | no data |
| North Saskatchewan River at Edmonton | July[3] | October | April | July[3] | October | January[4] |
| Lake Ontario at Ashbridges Bay | June | October | April | July | October | January |

[1] Criteria for selection of low- and high-risk months for invertebrates (*Ceriodaphnia dubia, Daphnia magna*):

Low risk:

- Summer month chosen due to lowest number of complicating stressors.
- For rivers, consideration also given to month with the highest flow based on data from HYDAT (Environment Canada, 1999b) for summer season to ensure maximum dilution.

High risk:

- Autumn month chosen due to high number of complicating stressors, such as limited sunlight and competition for dwindling food supplies.
- For rivers, consideration also given to month with the lowest flow based on data from HYDAT (Environment Canada, 1999b) during period of autumn when a high number of complicating stresses is anticipated.

[2] Each season is assumed to present equally high risks to chinook salmon. Therefore, one month is selected from each season. For rivers, months representing mean maximum and minimum flows were included in the selection to ensure that minimum and maximum dilution are considered.

[3] Month with 20-year mean maximum discharge (Environment Canada, 1999b).

[4] Month with 20-year mean minimum discharge (Environment Canada, 1999b).

salmon are lower than those for *C. dubia*. In the Don River, a 41% probability of 20% or greater mortality for chinook salmon at 1900 m from the source was forecasted for January. The forecasted risk dropped to its lowest in August (3% probability of 20% or greater mortality for chinook salmon at 1100 m from the source). For Lake Ontario, the highest risk was forecasted for January, at which time there was estimated to be a 3–40% probability of 20% or greater mortality to chinook salmon in a zone approximately 500 m wide and 3000 m long. In the North Saskatchewan River, a 52% probability of 20% or greater mortality to chinook salmon was forecasted in a narrow plume 1000 m from the source. This dropped to 4% probability of 20% or greater mortality to chinook salmon at approximately 4000 m from the source.

Although forecasted probabilities of risk for fish are lower than those for invertebrates, these may be important due to the longer period of time required for salmonids to regenerate. Therefore, lower probabilities of fish mortality may have population effects over the long term. Conversely, fish are mobile and have the ability to detect and avoid chloramine concentrations. Avoidance to chloramine has been reported at 0.05–0.11 mg/L for coho salmon and rainbow trout (Cherry *et al.*, 1979). The avoidance effects may be offset by conditions in the effluent (e.g., elevated ammonia concentration and

**FIGURE 10** Spatial distribution of risk for *Ceriodaphnia dubia* (Cd) and *Oncorhynchus tshawytscha* (Ot) exposed to inorganic chloramines discharged by Clover Bar Generating Station to the North Saskatchewan River: (a) and (b) August – Cd; (c) to (f) August – Ot (Moore *et al.*, 2000)

Figure 10a

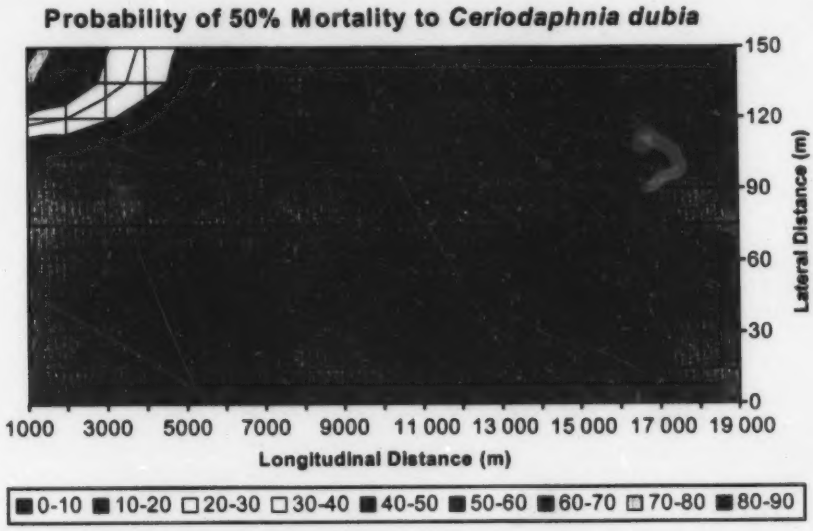
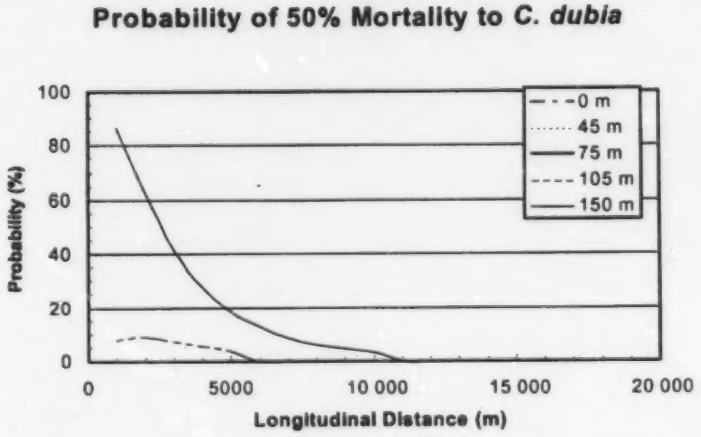



Figure 10b

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elevated water temperatures) that result in attraction. Data are not available to determine whether avoidance and/or attraction can affect the risk forecasts determined for this assessment.

The limited monitoring data for the Don River indicate that the river model may have overpredicted chloramine concentrations somewhat. The same is likely true for Lake Ontario, although the comparison is made difficult by differences in orientation between the modelled scenario plume and the monitored plume. No monitoring data are available for the North Saskatchewan River.

FIGURE 10 (continued)

Figure 10c

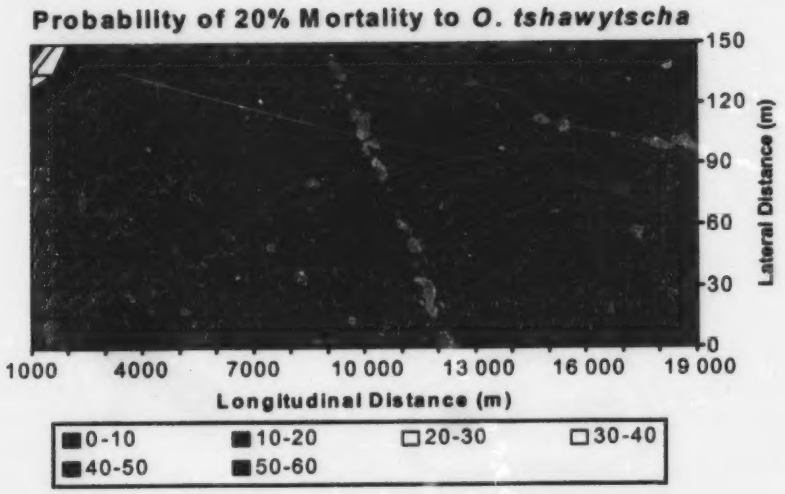
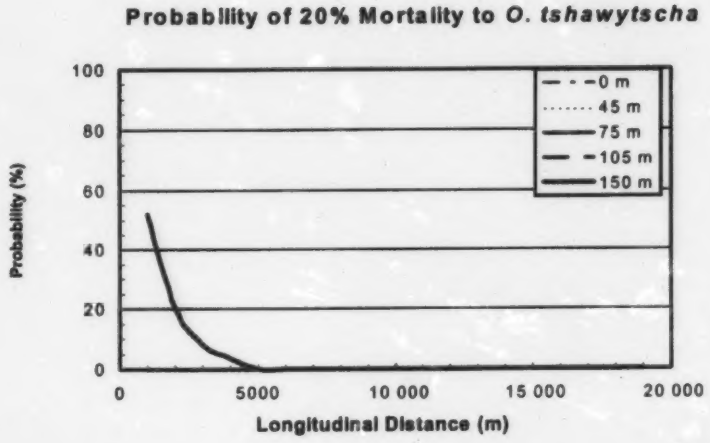



Figure 10d

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3.1.2.3 Uncertainty

There are several sources of uncertainty in this assessment. Many of these uncertainties are founded in the reliance on existing data produced using traditional analytical methods. The existing methods have not permitted accurate differentiation between the chlorine species. Usually concentrations pertaining to inorganic chloramine are expressed as TRC or CRC, rather than monochloramine, dichloramine or trichloramine. In addition, the traditional methods have been prone to chemical interferences from various other chemical species, which result in

**FIGURE 10** (continued)

Figure 10e

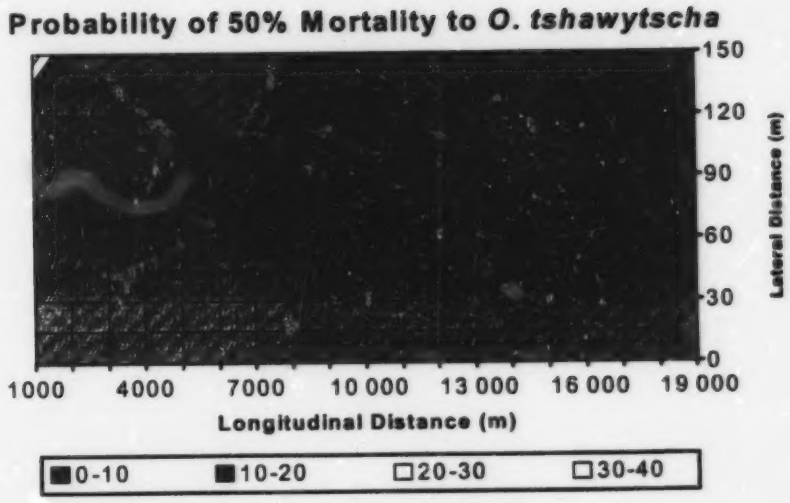
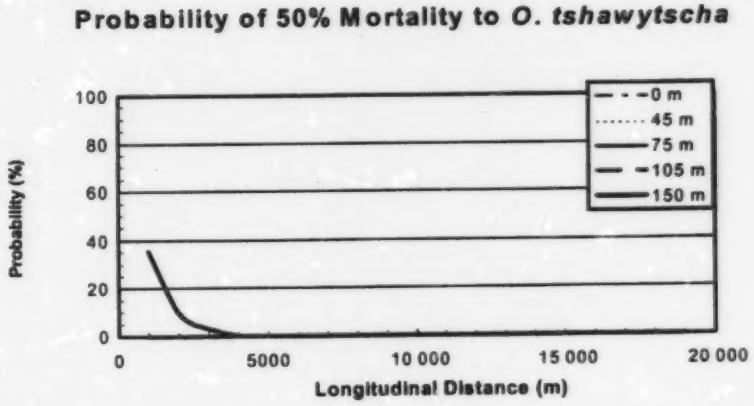



Figure 10f




false-positive measurements for various residual chlorine categories and congeners.

There is moderate uncertainty associated with production and loading estimates. Precise inorganic chloramine loading data are not available. Potable water, cooling water and wastewater treatment facilities typically measure chlorine residual as TRC and rarely conduct analyses for individual inorganic chloramine species. Therefore, in order to estimate exposure, it was necessary to assume that TRC concentrations were equal to inorganic chloramine concentrations. This may have resulted in overpredictions of inorganic chloramine concentrations in surface waters and conservative risk estimations.

The estimates for production and loading of chloramine from potable water include only

those utilities intentionally producing chloramine for disinfection purposes. In fact, these values will be higher, since chloramines may be unintentionally formed due to the concurrent presence of ammonia in treated water. Also, inorganic chloramine may be formed *in situ* in surface waters when there is a release of FRC to a surface water containing sufficient concentrations of ammonia. It is not possible to quantify risks associated with *in situ* chloramine production. Although there are no data available characterizing risk from such sources, there is no reason to believe that the impacts resulting from such sources would be different from those presented in this report for inorganic chloramines.

There is moderate to high uncertainty associated with characterizations of inorganic chloramine decay. Several studies are available in the open literature that quantify rates of residual chlorine loss from the water column; however, few differentiate between chlorine species. Some studies report monochloramine or FRC decay as TRC only, which can be problematic, since there are differences in the decay rates of FRC, inorganic chloramines and organic chloramines. FRC species are generally more reactive than inorganic chloramines, and there are limited data regarding the decay of organochloramine species. Given its compositional uncertainty, decay rates expressed as TRC will not be precise indicators of inorganic chloramine decay without further speciation. Another limitation of the existing residual chlorine decay data is that most of the established analytical methods falsely measure several compounds as chlorine residual (Johnson, 1978; Milne, 1991; Harp, 1995) (see Section 2.1.2). This shortfall has particular implications for the probabilistic risk modelling that was conducted.

Sensitivity studies show that decay becomes more important in estimating environmental concentrations with distance from the source of input. Therefore, predictions in the far-field will have greater uncertainty than those in the near-field. The distributions and selection of decay data for risk modelling, however, were based on the literature and professional judgment rather than on site-specific data. Thus, there are some subjective uncertainties in the case studies that could not be accounted for in the model simulations. To address these uncertainties, site-specific studies would be required. In addition, future *in situ* chloramine decay studies should examine the loss of chloramine to suspended and bed sediments and chloramine's fate associated with these sediments (i.e., resultant transformation products, potential for release back to the water column). The toxicity of sediment-associated chloramines and reaction products requires evaluation.

There is moderate uncertainty in the dispersion coefficients used for the conservative and probabilistic modelling of effluents and cooling waters. Dispersion coefficients are highly site specific, and they were not available for all the surface waters subjected to modelling. The sensitivity analysis demonstrated that the transverse mixing coefficient has a strong influence on the width and downstream extent of the chloramine plume. The distribution for this variable was, however, based on literature and professional judgment rather than on site-specific data. To address these uncertainties, site-specific studies would be required.

Systematic monitoring surveys at the case study sites and other sites near chloramine sources would provide further data regarding chloramine exposure and would facilitate an analysis of risk using actual data. Together, monitoring programs and model development can complement each other, since monitoring data allow for model validation and calibration. Validated and calibrated models can then be used as an alternative or to support monitoring. Such extensive monitoring data were not available for this assessment.

The toxicity assessment indicated that coho salmon and rainbow trout may be more sensitive than chinook salmon. Therefore, the environmental risk for fish as presented in this report may have been higher if a more sensitive fish species had been selected as the receptor. On the other hand, the forecasted risk to fish

may have been lower if a non-salmonid, such as bluegill (*Lepomis macrochirus*), had been chosen as the receptor.

In addition, the risk analysis did not involve the use of the entire concentration–response relationship; rather, the assessment was simplified by choosing 20% and 50% effect levels as endpoints. This was a practical consideration due to the number of exposure distributions (typically greater than 100) produced for each case study and the need to communicate risk in a direct manner. Toxicity data were also not adjusted for temperature. A discussion of temperature effects relevant to chloramine toxicity has been presented in a supporting document (see Farrell and Wan, 2000: Appendix A).

The approach taken in this assessment has been to examine risk to sensitive individual species and then to extrapolate effects to populations and ecosystems. This approach does not facilitate inferences regarding risk in the context of the community and does not describe indirect effects resulting via disruption of the food web. An evaluation of community-level risk would indicate the range of sensitivity that exists among individual species and would allow the ecological role of the more sensitive species to be better judged.

## 3.2 CEPA 1999 64(b): Environment upon which life depends

Although there are uncertainties regarding the fate of inorganic chloramines in the atmosphere, the available information shows that they would make a negligible contribution to tropospheric ozone formation and would not contribute at all to stratospheric ozone depletion.

## 3.3 Conclusions

CEPA 1999 64(a): Based on the available data, it has been concluded that inorganic chloramines in chlorinated effluents, cooling waters and treated potable water are entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the aquatic environment at various locations across Canada. Therefore, inorganic chloramines are considered to be "toxic" as defined in Paragraph 64(a) of CEPA 1999.

CEPA 1999 64(b): Based on the available data, it has been concluded that inorganic chloramines are not entering the environment in a quantity or concentration or under conditions that constitute a danger to the environment on which life depends. Therefore, inorganic chloramines are not considered to be "toxic" as defined in Paragraph 64(b) of CEPA 1999.

Overall conclusion: Based on the critical assessment of relevant information, inorganic chloramines are considered to be "toxic" as defined in Section 64 of CEPA 1999.

## 3.4 Considerations for follow-up (further action)

The largest releasers of inorganic chloramines to the Canadian environment are municipal wastewater facilities, followed by potable and cooling water sources. Efforts to manage risk should involve limiting the exposure in surface

waters from these sources. The chemistry of chloramines is extremely variable, and their persistence and fate will vary based on hydrological and climatic conditions, as well as water quality. Chloramine toxicity to freshwater and saltwater biota is also highly variable. As a result, reducing the exposure of aquatic biota to chloramines may involve an examination of regionally or locationally specific characteristics that affect chloramine risk. These would include decay, dilution and the presence of aquatic biota with sensitivity to inorganic chloramines.

The conservative-level assessment of chloramine-treated drinking water found that larger flows (e.g., from main breaks, punctures and large leaks, main flushing, and training of firefighters) destined for small streams with sensitive habitat can have devastating ecological consequences. However, low flow rate releases (e.g., from garden hoses or pinhole distribution system leaks) are unlikely to have any negative ecological consequences as long as the releases flow overland or via storm drains prior to entering a small stream.

Limiting exposure from unpredictable releases will prove most challenging. Reducing chloramine loading may be technologically feasible for point sources such as waste effluents or cooling waters, but not for geographically and temporally unpredictable releases from drinking water distribution systems. Regional-level control measures, potentially involving changes in treatment procedures, may have to be evaluated for regions with an abundance of aquatic environments that promote chloramine persistence, that provide low dilution and that contain sensitive aquatic ecosystems. Such measures must not compromise human health protection; selection of options must be based on optimization of treatment to ensure health protection, while minimizing or eliminating potential for harm to environmental organisms.

Although no existing marine or estuarine discharge scenarios were recommended for the probabilistic assessment, new discharges to marine and estuarine environments could produce negative ecological consequences. The marine environment contains aquatic organisms that are possibly even more sensitive to inorganic chloramines than freshwater species. Therefore, if a facility discharging chloramines to a marine environment is proposed, a precautionary risk assessment is recommended that evaluates site-specific characteristics that affect ecological risk.

Many of the input variables (e.g., effluent concentration, stream velocity) used in probabilistic modelling were based on limited data; hence, professional judgments were used to estimate distributions and to derive point estimates (e.g., transverse mixing coefficient and initial chlorine demand). Thus, there were several sources of uncertainty not accounted for in the analyses. Systematic monitoring studies at locations used as case studies for the probabilistic risk assessment and at other sites near chloramine sources would obviate the need for exposure modelling and allow for more confident predictions about risks of chloramines to aquatic biota in Canada. If it is determined in the risk management stage that comprehensive monitoring is required near chloramine sources, then consideration will need to be given to the standardization of a practical in-field sampling and analysis method that is able to distinguish between inorganic and organic chloramine species. If data (e.g., relevant to decay and transverse mixing) become available that may change risk forecasts, these should be considered, and the probabilistic assessment may need to be revisited.

Organic and inorganic chloramines are often found together; however, there are insufficient scientific data to allow an environmental risk assessment on the organic chloramine congeners to be conducted. In some instances, there may be a need to distinguish between inorganic and organic chloramine compounds for the purpose of risk management. As a unique group, existing analytical methods for organic chloramines would need improvement in order to allow measurement of individual congeners at the sub-microgram-per-litre level or to facilitate their measurement as a bulk

parameter. Research may be required to determine the prevalence and fate of organic chloramines versus inorganic chloramines in waters receiving either chlorinated or chloraminated discharges. This could involve spatial and/or temporal considerations due to the disproportionation of the various types of chloramine species over time. Environmental fate models would require revision with this information. Also, the toxicological characteristics of organic chloramines may require scrutiny. This could be an extensive task given the wide range of organic nitrogen compounds known to be present in natural waters and the fact that only a fraction of them are present as easily measured small molecules. Simple toxicological testing protocols for estimating the toxicity of mixtures of organic chloramines (or organic and inorganic chloramines) may require development, since it will not likely be practical or possible to routinely measure the many possible organic chloramine species that are likely to be present in these waters.

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# Appendix A Search Strategies Employed for Identification of Relevant Data

Data relevant to the environmental assessment of the entry, environmental fate and exposure, and environmental effects of chloramines were identified in original literature, review documents, and commercial and government databases and indices, including on-line searches conducted between January and May 1996 and during September 1998 of the following databases: Aqualine (Water Research Centre, Buckinghamshire; 1985–1996), ARET (Accelerated Reduction/Elimination of Toxics, Environment Canada; 1995), BIOSIS (Biosciences Information Services; 1990–1996), CAB (Commonwealth Agriculture Bureaux; 1990–1996), CCINFO (Canadian Centres Information On-line, Canadian Centre for Occupational Health and Safety; 1996), CESARS (Chemical Evaluation Search and Retrieval System, Ontario Ministry of the Environment and Michigan Department of Natural Resources; 1996), CHEMINFO (Canadian Centre for Occupational Health and Safety; 1996), CHRIS (Chemical Hazards Release Information System; 1996), Canadian Research Index (Government of Canada/Micromedia; 1990–1996), Current Contents (Institute for Scientific Information; 1990 – September 1998), ELIAS (Environmental Library Integrated Automated System, Environment Canada Library; January 1996), ENVIRODAT (Environment Canada; 1996), Enviroline (R.R. Bowker Publishing Co.; 1990–1996), Environmental Abstracts, Environmental Bibliography (Environmental Studies Institute, International Academy at Santa Barbara; 1975–1996), Envirosource (Environment Canada; 1996), GEOREF (Geo Reference Information System, American Geological Institute; 1990–1996), HSDB (Hazardous Substances Data Bank, U.S. National Library of Medicine; 1996), IRPTC (International Register of Potentially Toxic Chemicals, Geneva; April 1996), Life Sciences (Cambridge Scientific Abstracts; 1990–1996), MSDS (Material Safety Data Sheets, Canadian Centre for Occupational Health and Safety; 1996), NATES (National Analysis of Trends in Emergencies System, Environment Canada; 1996), Natural Resources Canada Headquarters Library (1996), Northern Info Network (1996), NPRI (National Pollutant Release Inventory, Environment Canada; 1990–1996), NTIS (National Technical Information Service, U.S. Department of Commerce; 1995), Pesticide Registrant Survey (Environment Canada and Agriculture Canada; 1996), Pollution Abstracts (Cambridge Scientific Abstracts, U.S. National Library of Medicine; 1990–1996), POLTOX (Cambridge Scientific Abstracts, U.S. National Library of Medicine; 1990 – September 1998), RTECS (Registry of Toxic Effects of Chemical Substances, U.S. National Institute of Occupational Safety and Health; 1996), Toxline (U.S. National Library of Medicine; 1990–1996), TRI93 (Toxic Chemicals Release Inventory, Office of Toxic Substances, U.S. Environmental Protection Agency; 1993), U.S. EPA – AQUIRE (U.S. Environmental Protection Agency; May 1995), U.S. EPA – ASTER (Assessment Tools for the Evaluation of Risk, U.S. Environmental Protection Agency; 1994), U.S. EPA – ECOTOX (Ecotoxicology, U.S. Environmental Protection Agency; May 1995), U.S. EPA – National Catalog (U.S. Environmental Protection Agency; 1996) and WASTEINFO (Waste Management Information Bureau, American Energy Agency; 1973–1995). Reveal Alert was used to maintain an ongoing record of the current scientific literature pertaining to the potential environmental effects of chloramines. Data obtained from the open literature after January 1999 were not considered in this assessment unless they were critical data received during the 60-day public review of the report (July 8 to September 6, 2000).

Surveys of municipal water treatment facilities and distribution systems and municipal wastewater treatment facilities were administered to all Canadian municipalities with populations ≥5000 to determine users, releases, environmental concentrations, effects or other data that were available to them for chloramines (Environment Canada, 1997b,c). In addition, a survey of Canadian industry was carried out under the authority of Section 16 of CEPA (Environment Canada, 1997d). Targeted companies with commercial activities involving more than 1000 kg of chloramine were required to provide information on users, releases, environmental concentrations, effects or other data that were available to them for chloramines.